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Degradation of PCBs in a Marine Sediment Treated with Ionizing and UV Radiation

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Radiolytic (electron beam) and photolytic (ultraviolet, UV) dechlorination of polychlorinated biphenyls (PCBs) in a marine sediment are described. Samples of a PCB-laden marine sediment, Standard Reference Material (SRM) 1944, New York/New Jersey Waterway Sediment, have been mixed with aqueous alcohol solutions and irradiated with an electron beam or photolyzed. Additives, such as alcohol, enhance the radiolytic yield and PCB dechlorination. In the electron beam irradiated samples, the concentrations of 29 PCB congeners decrease with irradiation dose. At the highest dose (500 kGy), the total concentration of PCBs is decreased by 83%. Photolysis leads to little dechlorination, but photolysis with added triethylamine leads to dechlorination (about 60%). It is likely that photolysis under optimal conditions (other additives, exposure time) may be as effective as electron beam radiolysis for the dechlorination of PCBs in sediment.

Introduction

The hydrophobic nature of polychlorinated biphenyl congeners (PCBs) leads to their eventual accumulation in aquatic sediment. Sediment contamination is an area of growing concern. Many U.S. waterways have serious problems related to pollution (*1*). In 1998, it was estimated that up to 7% of U.S. watersheds have polluted sediments to the extent where the potential for adverse effects is considered high (*2*). A high-profile example of a system with severe sediment contamination associated with PCBs is the Hudson River (*3*) and the surrounding watershed including the New York/New Jersey Harbor Estuary (*4*). Concentrations of PCBs on the order of 4700 ppm (μg g^{-1}) have been observed in sediment collected from the Upper Hudson River (*3*). The U.S. EPA has established a cleanup level of 1 ppm for PCB-contaminated sediment at several sites across the United States and less than 1 ppm at other sites to protect organisms residing within the sediment and also those species that may eat sediment-based prey (*3*).

Sediment is often dredged from harbors in an effort to provide the proper conditions for navigation. However, in some cases dredging may be expensive and argumentative when the sediment is PCB-laden or the dredging is proposed as a PCB cleanup method. The cleanup plan for the Upper Hudson River, in which it is recommended to dredge 2.65 million yd^3 of PCB-contaminated sediment from a 40-mi stretch of the river to remove an estimated 150 000 lb of PCBs (*5*), has been a controversy (*6*). The dredged sediment must be treated to reach acceptable levels of PCBs. Radiolysis methods have been shown to effectively dechlorinate PCBs in water (*7*), aqueous micellar systems (*8*, *9*), alcohols (*10*), isooctane (*11*, *12*), and transformer oil (*11–14*). Ultraviolet (UV) irradiation of PCB-laden transformer oils has also been shown to effectively dechlorinate PCB congeners (*14*). However, there is a paucity of studies concerning the radiolytic or UV degradation of PCBs associated with sediment. Dioxin-contaminated sediments have been effectively treated with γ-radiation (*15*, *16*). Off-line supercritical fluid extraction of PCBs from contaminated soil followed by γ-radiolysis has been shown to reduce a tetrachlorobiphenyl congener in association with soil (*17*). Similarly, the extraction of PCBs from soil followed by the flotation of the solvent and subsequent radiolysis of the floatant has been reported along with the radiolysis of PCBs associated with soil (*18*). The reaction scheme for the radiolytic dechlorination of PCBs in 2-propanol has been described (*19*). The UV treatment of liquid laboratory waste (*20*), PCBs in hexane (*21*), non-ortho-PCBs in 2-propanol (*22*, *23*), and other persistent chlorinated organic compounds, such as dioxins, in solid and liquid media has been demonstrated (*24–26*), although investigations of the UV degradation of sediment-associated PCBs have not been reported. In the present study, the degradation of PCB congeners associated with marine sediment by ionizing (electron beam) and UV radiation is examined in an attempt to reach PCB levels below 1 μg g^{-1}.

Although the radiation chemistry of aqueous solutions is well-established (*27*) and permits quantitative prediction of radiation effects, it is not possible to make such predictions for the nonhomogeneous systems used in this study (i.e., aqueous 2-propanol sediment slurries). However, a portion of the sediment-associated PCBs are extracted into the aqueous 2-propanol phase, and we can outline the degradation mechanisms that occur within this phase. Briefly, radiolysis of aqueous solutions leads to the production of hydrated electrons (e_{aq}^-), hydroxyl radicals ($^•$OH), and hydrogen atoms:

$$H_2O \rightarrow e_{aq}^-, \ ^•OH, H^•, H_3O^+, H_2O_2, H_2 \qquad (1)$$

with the following yields (in units of μmol J^{-1}): $G(e_{aq}^-) = G(H_3O^+) = G(^•OH) = 0.29$; $G(H^•) = 0.062$; $G(H_2) = 0.042$; $G(H_2O_2) = 0.082$. Hydroxyl radicals react with PCBs via addition to the phenyl rings to produce various isomeric PCB adduct radicals ($^•$ArCl(OH)). The ipso isomers (resulting from the addition of $^•$OH on the same carbon that bears a Cl atom) undergo very rapid elimination of HCl to form phenoxyl-type radicals:

$$ArCl + \ ^•OH \rightarrow \ ^•ArCl(OH) \rightarrow ArO^• + HCl \qquad (2)$$

Addition at the ipso positions is significant with highly chlorinated PCBs but becomes less likely as the degree of chlorination is diminished. However, because $^•$OH radicals are highly reactive with most other organic compounds, degrading trace contaminants by $^•$OH in a medium with a high background of organics is not efficient. On the other hand, the hydrated electron is a strong reducing agent whose

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reactivity depends on the availability of a suitable vacant orbital and does not react with saturated organic compounds such as hydrocarbons and alcohols. Rather, it is preferentially captured by PCB molecules. The carbon–chlorine bond breaks very rapidly through a dissociative electron capture process:

$$e_{aq}^- + ArCl \rightarrow Ar^\bullet + Cl^- \tag{3}$$
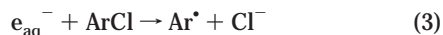
Hydrated electrons also react very rapidly (28) with oxygen ($e_{aq}^- + O_2 \rightarrow O_2^{\bullet-}$) and with the H^+ formed in the radiolysis ($e_{aq}^- + H^+ \rightarrow H^\bullet$). These reactions will compete with the dechlorination process but are easily prevented by purging the system with nitrogen and by adding alkaline buffers. Chloride ions, typically abundant in marine sediment, may be oxidized by $^\bullet OH$ radicals in acidic solutions to form $Cl_2^{\bullet-}$ radicals and then Cl_2. Both of these species may react with aromatic compounds to form chlorinated products, a reaction that would reverse the desired dechlorination process. However, this is easily prevented by the addition of an $^\bullet OH$ radical scavenger like 2-propanol.

PCBs that remain in association with or within the sediment phase may undergo dechlorination by thermalized electrons that may be formed at particle sites. However, the yield of such electrons is expected to be relatively low, and because of their limited mobility, they are effective only when produced in the immediate vicinity of the PCB molecule. Direct effect of radiation on the PCBs (i.e., the deposition of ionizing energy directly onto a PCB molecule), whether in the liquid or the solid portion of the slurry, can also lead to dechlorination. The contribution of such a process, however, is very low (16) since the ionizing energy is indiscriminately absorbed in all the medium molecules.

In contrast with ionizing radiation, UV light is absorbed by specific molecules, and its effect may be more selective. Direct light absorption by the PCBs will produce excited states that may be quenched by a reductant and undergo dechlorination. A reductive quencher that was used (14) in PCB-laden oil is triethylamine:

$$ArCl^* + Et_3N \rightarrow Ar^\bullet + Cl^- + Et_3N^{\bullet+} \tag{4}$$

Excited states of non-chlorinated organic compounds may be reduced to radical anions, which may transfer an electron to PCBs if the reduction potential of the compound is more negative than that of the chlorinated molecule. For example, with aromatic hydrocarbons:

$$ArH^* + Et_3N \rightarrow ArH^{\bullet-} + Et_3N^{\bullet+} \tag{5}$$

$$ArH^{\bullet-} + ArCl \rightarrow ArH + Ar^\bullet + Cl^- \tag{6}$$
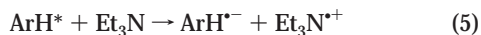
The present results show that both photolysis and radiolysis lead to dechlorination of PCBs in sediment slurries, although the efficiency is clearly less than that found with homogeneous phases.

Experimental Section

Experiments were carried out with Standard Reference Material (SRM) 1944. This is a dry marine sediment reference material, collected from New York/New Jersey waterways. The sediment has a median particle diameter (dry) on the order of 135 μm and is well-characterized for a range of PCB congeners (naturally present in the material) (29, 30). Comparison of a gas chromatogram for this material (e.g., Figure 3) with those for several Aroclors suggests that this SRM contains PCB congeners from a mixture of Aroclors 1232, 1242, 1248, and 1254. The total organic carbon in this material is $(4.4 \pm 0.3)\%$ (mass fraction) (29). Samples ($\approx$3 g)

of SRM 1944 were mixed with 30 mL of 1:1 (v/v) aqueous/organic medium before treatment. The aqueous medium contained 5 mmol L^{-1} sodium carbonate/bicarbonate buffer at pH 10.3 to neutralize the acid produced upon dechlorination.

Electron Beam Irradiation. Samples of SRM 1944 in aqueous buffer/2-propanol solutions were purged for 15 min with N_2 to remove oxygen and then irradiated under continuous mixing. Electron beam irradiation was performed using the University of Maryland Varian linear accelerator, which delivers 3-μs pulses of 7 MeV electrons at a dose rate of 10 Gy/pulse. The following doses were applied to triplicate samples: 0, 10, 50, 100, 200, and 500 kGy. Radiation dosimetry was performed using radiochromic films.

UV Irradiation. Three samples of SRM 1944 in aqueous buffer/2-propanol media were prepared as described above. One sample was exposed to UV light (300-W Xe lamp) for 115 h, and two were stirred for the same time without exposure to light; these were used to determine the concentrations of PCB congeners in the nonexposed 2-propanol/sediment slurry. In addition, three samples of SRM 1944 were mixed with water/2-propanol/triethylamine (3:2:1 v/v/v). One sample was exposed to the UV light for 115 h as above, one was stirred without photolysis but under room light, and one was stirred in the dark. The latter was used to determine the concentrations of PCB congeners in the nonexposed triethylamine/sediment slurry. Photolysis was carried out under continuous stirring in a Pyrex bulb, cooled by a water jacket to keep the temperature of the samples near 21 °C. The UV source was a 300-W Xe lamp placed 10 cm away from the front of the bulb.

Determination of Biphenyl and PCB Congener Concentrations. The aqueous layer of each electron beam irradiated sediment sample was decanted, and the sediment portions were pressurized fluid extracted (31) with hexane and acetone (50:50 v/v). A weighed aliquot of a gravimetrically prepared internal standard solution of octachloronaphthalene (OCN) was added to each sample prior to extraction. Activated copper was added to each sediment extract to remove elemental sulfur. The extracts were concentrated to approximately 0.5 mL using an automated evaporation system under N_2. The concentrated extracts were passed through silica solid-phase extraction (SPE) cartridges with 15 mL of 10% methylene chloride in hexane (v/v) and concentrated to approximately 0.5 mL as above. Calibration solutions consisting of SRMs 2262 (32) and 2274 (33) and three control samples, SRM 1944 as received, were also extracted using the same conditions described above. The aqueous portions of the ionizing radiation samples were extracted three times by liquid–liquid partitioning with 20-mL aliquots of hexane. The aliquots were concentrated to approximately 0.5 mL, passed through silica SPE cartridges with 15 mL of 10% methylene chloride in hexane (v/v), and concentrated to a final volume of approximately 0.5 mL. These concentrated aliquots were combined with the sediment extracts. The combined extracts and calibration solution extracts were fractionated on a semipreparative aminopropylsilane liquid chromatographic (LC) column (to isolate the PCB congeners and several lower polarity pesticides). Eluants were concentrated to approximately 0.5 mL under nitrogen, processed through aminopropyl SPE cartridges with 10 mL of hexane, concentrated as described above, and transferred to autosampler vials. The extracts were analyzed for the determination of the concentrations of PCB congeners using gas chromatography with mass spectrometry (GC/MS) with a relatively nonpolar column (DB-XLB, 60 m × 0.25 mm × 0.25 μm). The major ions monitored were 222, 258, 292, 326, 360, 394, 426, 464, 498, and 404. Three point calibration response curves with a zero intercept were constructed for

TABLE 1. Concentrations (ng g^{-1}) of Compounds in Irradiated Samples of SRM 1944, New York/New Jersey Waterway Sediment[a]

no.[b]	sub. pattern	0 kGy[c]	500 kGy[c]	%[d]	TEA non-UV[e]	TEA UV[e]	%[d]	ISO non-UV[f]	ISO UV[f]	%[d]
8	2,4′-	34.4	24.7 (1.0)	28	20.6	33.2	−61	24.9	87.0	−249
18	2,2′,5-	78.3	29.2 (2.1)	63	58.0	70.6	−22	62.7	192	−206
31	2,4′,5-	102	30.7 (6.0)	70	75.3	67.7	10	86.3	139	−61
28	2,4,4′-	110	21.8 (4.9)	80	87.5	44.9	49	116	141	−22
52	2,2′,5,5′-	112	28.8 (3.9)	74	84.6	134	−59	85.9	171	−99
49	2,2′,4,5′-	95.2	14.5 (2.2)	85	60.4	34.9	42	60.9	98.8	−62
44	2,2′,3,5′-	93.5	26.5 (3.3)	72	64.6	47.2	27	63.2	117	−85
66	2,3′,4,4′-	77.4	10.3 (1.7)	87	71.0	13.6	81	76.4	81.9	−7
95	2,2′,3,5′,6-	68.1	8.0 (3.3)	88	60.8	27.5	55	54.5	91.5	−68
101	2,2′,4,5,5′-	76.0	11.8 (1.9)	84	84.6	13.4	84	86.1	138	−61
99	2,2′,4,4′,5-	33.9	4.0 (0.6)	88	43.4	3.8	91	44.5	55.3	−24
87	2,2′,3,4,5′-	35.0	3.7 (1.0)	89	g	g	g	g	g	g
110	2,3,3′,4′,6-	89.2	8.0 (1.5)	91	g	g	g	g	g	g
118	2,3′,4,4′,5-	59.8	8.1 (1.9)	86	71.6	2.8	96	71.0	70.4	1
105	2,3,3′,4,4′-	30.4	3.6 (1.0)	88	28.6	1.8	94	30.3	28.9	5
151	2,2′,3,5,5′,6-	19.1	<1[h]	>95	g	g	g	g	g	g
149	2,2′,3,4,5′,6-	67.1	4.2 (0.7)	94	66.1	4.1	94	64.0	77.5	−21
153[i]	2,2′,4,4′,5,5′-	88.3	6.3 (1.4)	93	88.6	2.6	97	97.4	90.1	8
138	2,2′,3,4,4′,5′-	75.4	5.5 (2.4)	93	89.8	1.1	99	106	83.1	21
128	2,2′,3,3′,4,4′-	9.3	no signal	100	15.0	no signal	100	12.1	13.9	−15
156	2,3,3′,4,4′,5-	7.7	<1	>87	9.9	no signal	100	13.5	6.5	52
187	2,2′,3,4′,5,5′,6-	29.3	<2	>93	34.4	no signal	100	37.6	27.5	27
183	2,2′,3,4,4′,5′,6-	13.6	<1	>93	g	g	g	g	g	g
180	2,2′,3,4,4′,5,5′-	46.4	<4	>91	58.1	no signal	100	70.1	35.3	50
170	2,2′,3,3′,4,4′,5-	21.2	<1	>95	30.9	no signal	100	29.4	16.7	43
195	2,2′,3,3′,4,4′,5,6-	<6	no signal	100	2.1	no signal	100	8.7	0.8	90
194	2,2′,3,3′,4,4′,5,5′-	<11	no signal	100	4.0	no signal	100	20.5	7.0	66
206	2,2′,3,3′,4,4′,5,5′,6-	9.8	<1	>90	13.3	no signal	100	16.8	5.8	65
209	decachloro-biphenyl	8.6	<0.15[j]	>98	3.7	no signal	100	16.4	0.9	95
	biphenyl	170	319 (4)	−88	200	307	−54	317	266	16
	∑PCBs, $n = 29$[k]	1508	261	83						
	∑PCBs, $n = 25$[k]	1351	247	82	1227	503	59	1354	1776	−31

[a] SRM 1944 described in ref 29. [b] PCBs are numbered according to the scheme by Ballschmiter and Zell (35) and later revised by Schulte and Malsich (36) to conform with IUPAC rules. [c] Electron beam irradiated samples of sediment slurries with 2-propanol. Values are the means of the mean of two injections of each of two samples at 0 kGy and three samples at 500 kGy. Values in parentheses are the standard deviations of the means of two injections of each of three samples (500 kGy). [d] Percent of PCB lost (+) or produced (−) relative to the unirradiated (0 kGy or non-UV) samples calculated as 100 − ([irradiated]/[nonirradiated] × 100). [e] UV-irradiated samples of sediment slurries with 2-propanol and triethylamine. Values are the means of the mean of two injections of one sample (covered) for the non-UV column and one sample for the UV column. [f] UV-irradiated samples of sediment slurries with 2-propanol. Values are the means of the mean of two injections of each of two samples for the non-UV column and one sample for the UV column. [g] These congeners were not measured in the UV-related samples. [h] Less than values are concentrations calculated from a very small response or peak close to the baseline. [i] PCB 132 may be coeluting with PCB 153. [j] Three times the standard deviation of the baseline noise. [k] Sum of 29 congeners listed for the electron beam irradiated samples (see Figure 1). Sum of 25 congeners determined in the UV-related samples as compared to the that of the same 25 congeners in the electron beam irradiated samples.

each PCB congener to generate response factors relative to OCN. The average of two calibrants was used for the determination of the concentration of PCB 128 based on the analysis of the control material. For the determination of the concentration of PCB 194 at 100 kGy and PCBs 206 and 209 at 200 kGy, only two samples were used (in each case an outlier was removed). The concentrations of PCBs determined in the control material SRM 1944 were similar to the concentrations reported on the SRM 1944 Certificate of Analysis. The percent differences between the reported and measured values ranged from 1% (PCB 52, see Table 1 for PCB numbering information) to 30% (PCB 8) and on average was 14%. No corrections for the recovery (100%) of PCBs in the control material were calculated for the electron beam samples. For the determination of the concentration of biphenyl, three solutions of biphenyl were used to calculate a single-point response factor of biphenyl relative to perdeuterated biphenyl that had been added to each electron beam irradiated and nonirradiated sample as an external standard. The biphenyl calibration solutions were not extracted or processed (i.e., fractionated on the LC column) alongside the samples. Biphenyl is not fully retained on the LC column during the fractionation procedure described above; only about 10% is recovered based on the analysis of the control material SRM 1944. Therefore, concentrations of biphenyl measured in the electron beam irradiated and

nonirradiated samples were corrected for the recovery (100%) of biphenyl in the control material SRM 1944.

For the determination of the concentrations of PCB congeners in the photolyzed sediment slurries, four PCB calibration solutions, consisting of weighed aliquots of SRMs 2262 and 2274 and a gravimetrically prepared solution of biphenyl, were prepared to use as calibrants. In addition, an internal standard solution of perdeuterated biphenyl and the following ^{13}C-labeled PCB congeners was prepared and gravimetrically added to the sediment and aqueous portions of the samples and to the calibration samples for quantification of biphenyl and PCB congeners: [^{13}C]-PCB 28, [^{13}C]-PCB 52, [^{13}C]-PCB 118, [^{13}C]-PCB 105, [^{13}C]-PCB 138, [^{13}C]-PCB 180, and [^{13}C]-PCB 209. Extraction procedures for the sediment portions of the samples were the same as described for the electron beam samples, although the sediment was dried with Na_2SO_4 and methylene chloride was the solvent. The aqueous portions of the samples were extracted three times by liquid−liquid partitioning with 20-mL aliquots of hexane. Following each liquid−liquid partitioning step, the samples were agitated for approximately 20 s and sonicated for approximately 12 min. The solvent portion of the samples were removed and concentrated to about 0.5 mL using the automated evaporation system mentioned above. The concentrated extracts were passed through silica SPE cartridges with 2 × 20 mL of 10% methylene chloride in hexane (v/v)
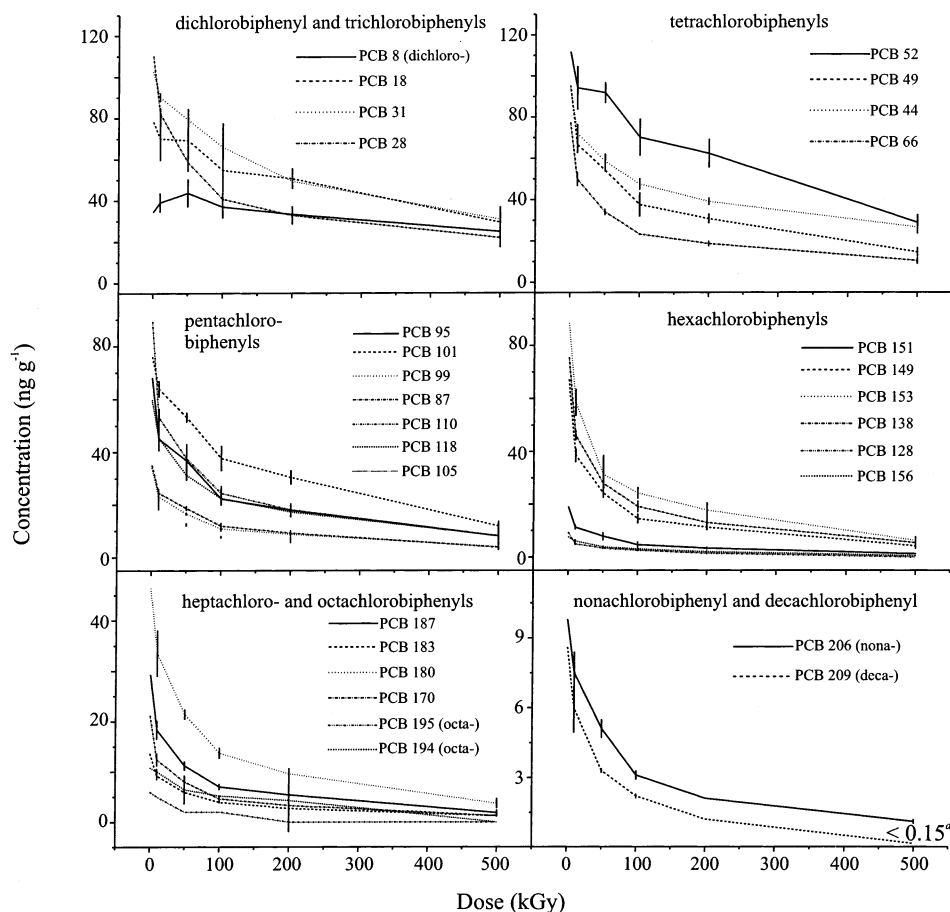
FIGURE 1. Concentrations (ng g⁻¹) of PCB congeners in electron beam irradiated slurries of SRM 1944 (New York/New Jersey Waterway Sediment) (*29*) as a function of dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy) and the standard deviation (*n* = 3, represented by an error bar) were calculated. Data from Table 1 (0 and 500 kGy) and Supporting Information Table 1. Key: *a*, value is three times the standard deviation of the baseline noise.

and concentrated to a final volume of approximately 0.5 mL. The aqueous samples, the sediment extracts, and the calibration samples (extracted alongside the sediment samples, one in duplicate) were analyzed by GC/MS. Three samples of a wet sediment reference material, Marine Sediment XI (*34*), were analyzed as a control material for the UV-related samples. The percent difference between the reported and measured values ranged from 30% (biphenyl) to 67% (PCB 209) and on average was 50%. Analyte concentrations in the UV-related samples were corrected for the recovery (100%) of each compound in the control reference material.

Results and Discussion

Electron Beam Radiolysis. PCB-laden sediment samples mixed with an aqueous alcohol solution were 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
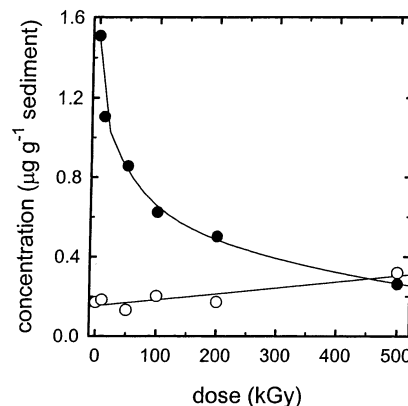

FIGURE 2. Concentration (μg g⁻¹) of PCBs (●) (Σ29 congeners, Table 1) and biphenyl (○) in electron beam irradiated samples of SRM 1944 (described in Figure 1) as a function of dose (kGy). For each dose, the means of the mean of two injections of each of two (0, 50, and 100 kGy) or three (200 and 500 kGy) samples was calculated. Data from Table 1 (0 and 500 kGy) and Supporting Information Table 1.

a function of dose (Figure 1). The initial (0 kGy) and final (500 kGy) concentrations of each PCB congener and biphenyl are listed in Table 1 along with the percent decrease at 500 kGy. A dose of 500 kGy destroyed most (about 83%) of the total PCB concentration in the sediment (Figure 2) (i.e., the concentration of the sum of 29 PCB congeners decreased from 1.5 to 0.26 μg g⁻¹). The concentration of biphenyl increased with dose (Table 1, Figure 2). The concentration
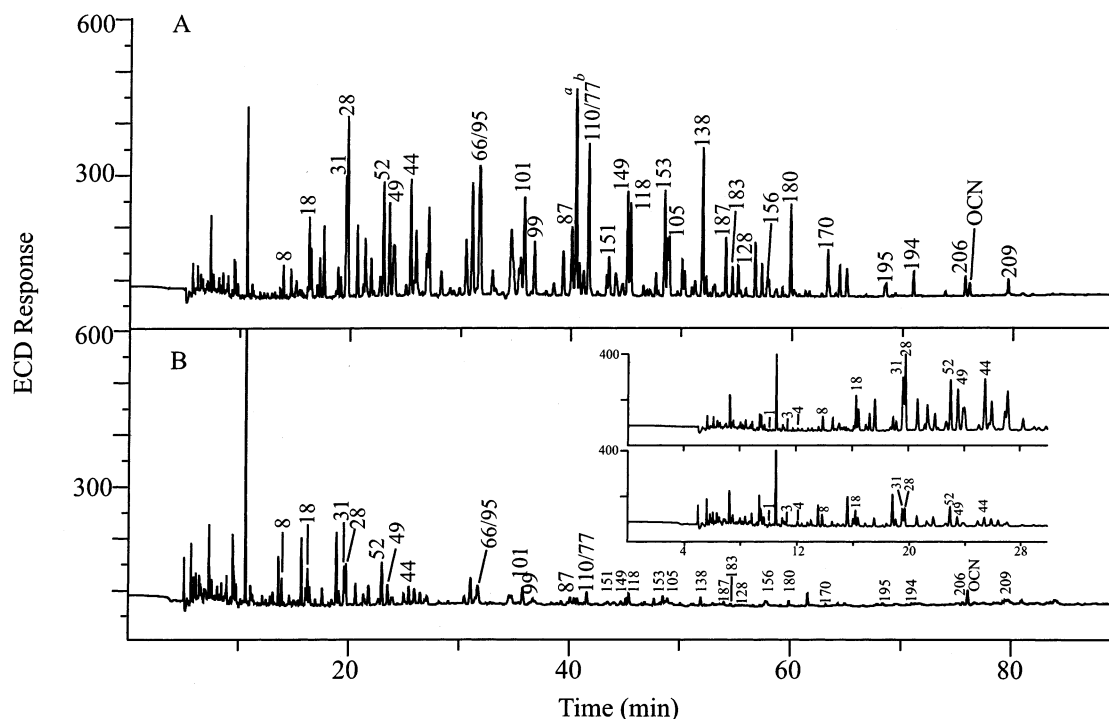
FIGURE 3. Gas chromatograms (5% phenyl methyl polysiloxane capillary column, 60 m × 250 mm, 0.25 μm film) with electron capture detection of (A) an unirradiated and (B) irradiated (500 kGy) slurry of SRM 1944 (New York/New Jersey Waterway Sediment) (*29*). Insert in panel B compares several mono-, di-, tri-, and tetrachlorobiphenyls in the unirradiated and 500 kGy sediment extracts (PCBs 1, 3, and 4 are 2- and 4-chloro- and 2,2′-dichlorobiphenyl; see Table 1 for other PCB structures). Key: *a*, 4,4′-DDE present in SRM 1944 (*29*) also degrades via electron beam irradiation; *b*, PCB congener 77 (3,3′,4,4′-tetrachlorobiphenyl) may be coeluting with PCB congener 110.

of other PCB congeners, which may be present in the sediment at much lower concentrations than those examined, were not determined. We assume that the congeners measured are representative of most of the PCBs in the sediment slurries based on the examination of gas chromatograms of the unirradiated material generated using an electron capture detector (GC-ECD, Figure 3A). A portion of monochlorobiphenyls (1-, 2-, 3-) and dichlorbiphenyls other than 2,4′- (PCB 8) that were likely produced as intermediate products may also be present in the sediment at 500 kGy, although these were not measured. The slight increase in the concentration of PCB 8 at 500 kGy relative to that measured at 0 kGy supports this hypothesis (Figure 1, Table 1). However, an examination of a GC-ECD chromatogram of a 500 kGy sample extract shows that the lower molecular weight byproduct concentrations are negligible (Figure 3B). For example, GC-ECD peaks for PCB congeners 1 (2-), 3 (4-), and 4 (2,2′-), which are barely present in the unirradiated sample, are only just above the baseline in the irradiated sample (insert of Figure 3B). Interestingly, the degradation of 4,4′-DDE is revealed upon examination of the GC-ECD chromatograms of unirradiated (0 kGy) and irradiated (500 kGy) SRM 1944 (Figure 3). This provides evidence of the dechlorination of other halogenated organic compounds in sediment; further assessment of the degradation of chlorinated pesticides by electron beam is underway.

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 1.3×10^{-11} mol J^{-1}. By comparison with the radiolytic yield of e$_{aq}^{-}$ in aqueous alcohol solutions (*27*), 2.7×10^{-7} mol J^{-1}, our observed dechlorination yield is lower by 4 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 (*29*). 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 solvated electrons, the electrons decay by reacting with other compounds or other radicals, including self-reaction. Reactions of e$_{aq}^{-}$ with H$^{•}$ atoms and $^{•}$OH radicals are prevented by the use of 2-propanol, which reacts with both of these species rapidly (*28*). Scavenging of e$_{aq}^{-}$ by the protons formed upon radiolysis is prevented by the use of the carbonate buffer, which keeps the solution at pH > 7. However, the sediment contains other compounds that may react with e$_{aq}^{-}$ and decrease the dechlorination yield, such as transition metal ions, nitrate or nitrite ions, and unsaturated organic compounds. For example, if we assume that 10% of the metal ions in the SRM 1944 (*29*) are extracted into the aqueous phase, we estimate the concentrations of the most abundant ions as follows: [Zn^{2+}] = 0.15 mmol L^{-1}, [Pb^{2+}] = 0.024 mmol L^{-1}, [Cr^{3+}] = 0.077 mmol L^{-1}, and [Mn^{2+}] = 0.14 mmol L^{-1}. Since all of these ions react with e$_{aq}^{-}$ very rapidly (*28*) and since these assumed concentrations are higher than the concentrations of PCBs, it is likely that a large fraction 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 a PCB molecule. The effect of these metal ions and other electron scavengers cannot be quantified from available data but apparently is severe.

In summary, the electrons produced by radiolysis of the liquid phase have a very low probability to lead to PCB dechlorination. Any ionizing radiation absorbed in the solid phase produces secondary electrons (*27*), which are not
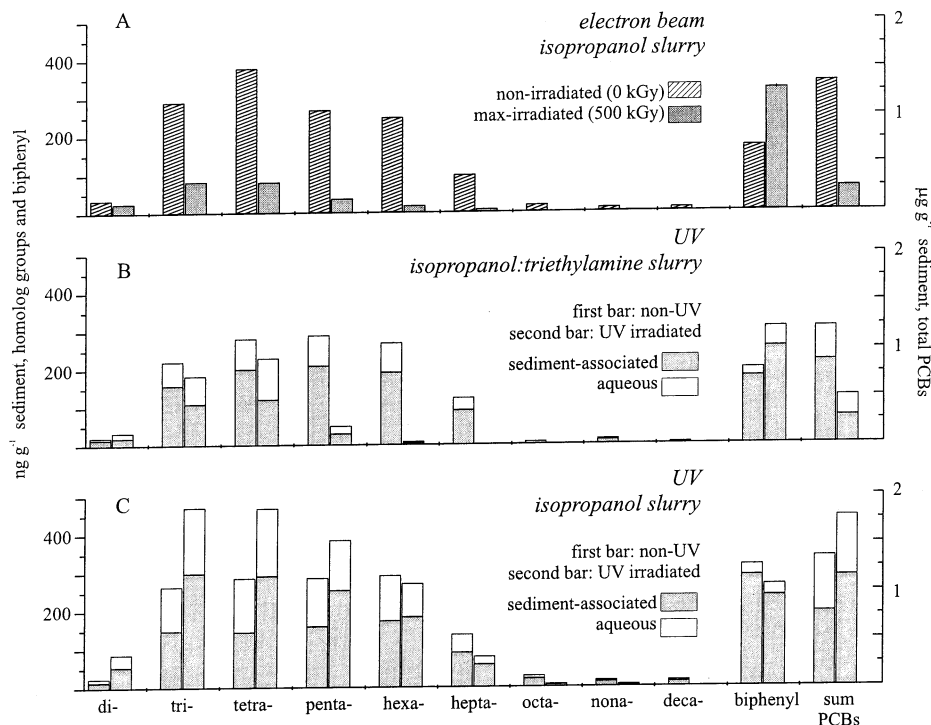
FIGURE 4. PCB homologue and biphenyl concentrations in (A) unirradiated ($n = 2$, 0 kGy) and irradiated ($n = 3$, 500 kGy) 2-propanol sediment slurries of SRM 1944 (New York/New Jersey Waterway Sediment) (29) and nonphotolyzed (UV) and photolyzed sediment slurries of SRM 1944 in (B) 2-propanol and triethylamine (one sample [covered] non-UV and one UV) and (C) 2-propanol (two samples [not covered] non-UV and one UV). The distribution of PCBs between aqueous and sediment phases is shown for the UV-related samples. Total PCBs is the sum of 25 PCB congeners (Table 1).

TABLE 2. Concentrations (Sediment-Associated plus Aqueous) of PCB Homologue Groups in Nonphotolyzed Sediment Slurries

no. of Cl[a]	total[b] TEA[c] not covered	% sediment-associated	total TEA covered	% sediment-associated	total ISO no. 1[d]	% sediment-associated	total ISO no. 2[d]	% sediment-associated
di	24	51	21	72	23	63	27	57
tri	227	41	221	71	247	58	282	54
tetra	293	42	281	71	260	51	313	50
penta	243	36	289	72	261	55	312	55
hexa	228	33	269	72	266	60	319	59
hepta	97	34	123	73	124	66	150	66
octa	11	0	6	0	27	73	31	71
nona	7	0	13	74	16	76	17	75
deca	6	0	4	0	15	72	18	72
sum[e]	1136	37	1227	71	1240	58	1468	57

[a] Homologue groups (number of chlorines). [b] Total PCB homologue concentration (ng g^{-1}) in the sediment and aqueous phases. [c] Aqueous slurry with triethylamine and 2-propanol; one kept under room light and one covered with foil. [d] Aqueous slurry with 2-propanol; each not covered. [e] Sum of 25 PCB congeners (Table 1).

mobile and are likely to react with PCBs only if the molecules happen to be at the site of the electron production. Because of these limitations, it was decided to study the effect of UV irradiation on such systems. While the electrons produced by radiolysis can be scavenged by other components, the UV light is expected to be absorbed directly by PCB molecules. In addition, if all of the excited states can be reduced by proper quenchers (i.e., additives such as alcohols or amines), the reaction may selectively lead to dechlorination. Of course, some of the UV light may be absorbed by other organic compounds. The fraction absorbed by aromatic hydrocarbons will produce radical anions that can transfer an electron to a PCB molecule, but the fraction of light absorbed by other compounds will be lost. Further details of the photolytic reactions have been summarized (14). The main disadvantage of the UV photolysis, as compared with the electron beam radiolysis, is that its penetration is limited to the liquid phase and the exposed surface of the solid phase. Nevertheless,

photolysis can be also an effective method for the dechlorination of PCBs in association with sediment as described below.

UV Photolysis. Samples were photolyzed in two different media: (a) identical to the mixtures used for radiolysis and (b) similar conditions but with 5 mL of the alcohol being replaced with triethylamine (TEA). Samples of both types were photolyzed by a UV lamp; sample a enables a direct comparison with the radiolysis experiment and sample b demonstrates the effectiveness of TEA, which is a better reductive quencher than 2-propanol. Indeed, when we compare the photolyzed and nonphotolyzed samples (see below, Figure 4), we find a considerable decrease in the concentrations of PCBs in the presence of TEA but little change in the absence of TEA.

A comparison of the concentrations of PCB homologue groups measured in the TEA sediment slurry that was photoloyzed to those measured in the electron beam

irradiated slurries (Figure 4, Table 1) suggests that photolysis for 115 h is less efficient than radiolysis at a dose of 500 kGy for the dechlorination of PCBs but is about as efficient as radiolysis at a dose of 200 kGy (Figure 2). Photolysis with TEA leads to the practical disappearance of the PCB congeners with 5 or more chlorines, similar to the radiolysis results, but the concentrations of those with 3 or 4 chlorines are decreased for some congeners but increased for others (Table 1). The electron beam radiolysis of the sediment slurry led to a reduction in all of these congeners. The dichlorobiphenyl (PCB 8, Table 1), which decreased slightly under radiolysis, was increased by photolysis. This comparison shows that photolysis selectively dechlorinates higher molecular weight congeners. We expect that further treatment by electron beam or UV light will lead to the complete dechlorination of sediment-associated PCBs.

It is interesting to note the difference between the results found with the nonphotolyzed TEA sediment slurries that were kept either under room light or in the dark, both being stirred for 115 h in parallel with the photolyzed sample. In general, the PCBs were more efficiently extracted into the aqueous phase under light (Table 2). The total PCB concentration (Σ25 congeners) in the TEA aqueous phase was 63% (37% sediment-associated) in the sample kept under light in comparison to 29% (71% sediment-associated) for the sample protected from light. In contrast, the concentrations of PCBs (total) associated with the two sediment slurries prepared in the absence of TEA (both not covered) were <50% in the aqueous phase (Table 2). Sediment-associated PCBs in the presence of TEA were ultimately extracted more efficiently into the aqueous phase under light conditions, and in the absence of TEA, the PCBs remain largely sediment associated. Ambient light may have enough energy to penetrate particle surfaces, and as a result, other organic components in the sediment are photolyzed in the presence of TEA. Decomposition of organic matter could lead to the release of PCBs bound to the sediment that are otherwise nonexchangeable with the aqueous phase and/or are undetected via solvent extraction.

Interestingly, photolysis in the absence of TEA leads to a decrease in the concentrations of PCB congeners with 6 or more chlorines but an increase in the concentrations of those with 2−5 chlorines (Figure 4). The photolysis is much less effective than that in the presence of TEA, although it is expected that photolysis for longer times will lead to further dechlorination. It is noted, however, that the total concentration of PCBs (Σ25 congeners determined in the UV-photolyzed samples, Table 1) is slightly increased rather than decreased (Figure 4). This effect is likely masked in the photolyzed sample by the increased rate of dechlorination and may again be due to the photolysis of other organic components in the sediment. We plan to examine this effect further by photolyzing sediment slurries with different additives.

Practical Considerations. The results and analyses reported here form the basis of a sound understanding of the effects produced by radiolytic and photochemical methods for destruction of sediment-associated PCBs. Although we have analyzed only PCBs, it is clear from the discussion that other compounds present in the sediment also can be reduced by the radiolytic or photolytic treatment. Other chlorinated organic compounds are dechlorinated, and transition metal ions may be reduced and possibly precipitated. The specific methods employed in this work, however, are limited in their practical application. A combination of dredging and subsequent treatment by means of such methods, especially with relatively expensive and unacceptably toxic additives, would be considered only in highly special cases. Some revisions, however, may justify greater practical interest. As an example, the use of lime for pH

adjustment and substitution of benign substances (such as ascorbate) for the alcohol and the amine could make radiation or photochemical processing of sediments into a competitive technology. Experiments are underway to test compounds of potential applicability. Moreover, the photochemical efficiency can be increased by an order of magnitude or more by eliminating the Pyrex 300- nm cutoff (i.e., using a quartz window or a windowless configuration), using a better UV source, and improving the irradiation geometry. These parameters are also under study.

Supporting Information Available

One table detailing the concentrations of compounds in iradiated samples of SRM. This material is available free of charge via the Internet at http://pubs.acs.org.

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