DDE in Sediments of the Palos Verdes Shelf, CA: *In Situ* Transformation Rates and Geochemical Fate

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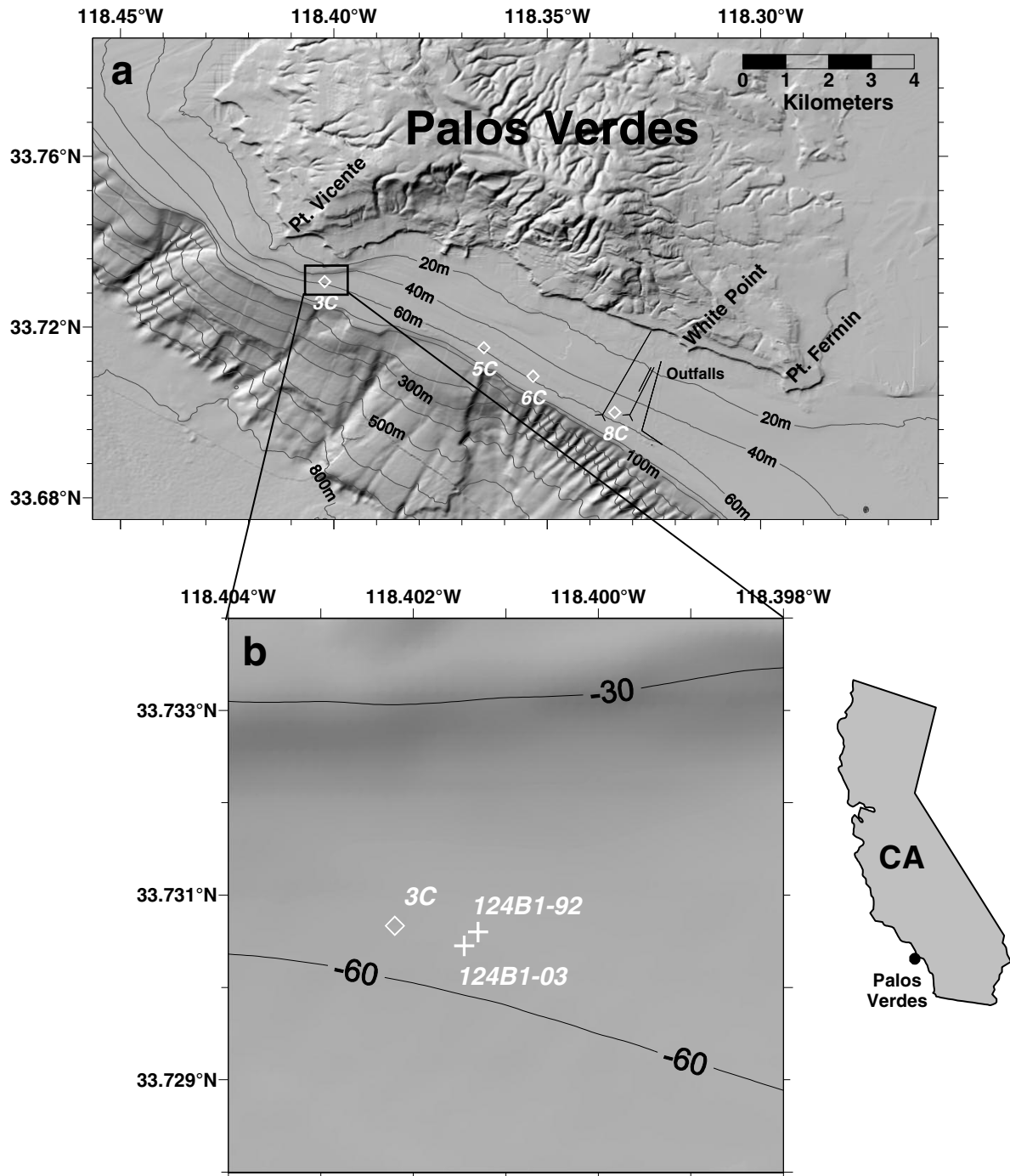
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Supporting Information

1. Sampling Locations

Figure S1: Maps showing: (a) Palos Verdes Shelf and LACSD coring stations, and (b) locations where LACSD station 3C and USGS cores were collected.

2. Transformation Pathways of DDT

DDT can be transformed abiotically and through microbially mediated reactions. Figure S2 presents a generalized scheme of potential pathways for microbial degradation of DDT based on findings from a combination of studies involving pure cultures. The reactions depicted in this figure have not been verified for all systems and probably represent an oversimplification of the range of possible reactions that can occur in individual species and/or environments. The predominant DDT metabolite in PVS sediments is *p,p'*-DDE. This compound is believed to have been formed through hydrolytic and/or microbial dehydrochlorination shortly after discharge from the LACSD outfall system. Under the reducing conditions that prevail in all but the upper few centimeters of the sediments on the PVS, *p,p'*-DDE could be transformed by reductive dechlorination (to form *p,p'*-DDMU) or by hydrogenation (to form *p,p'*-DDD). As shown in Figure S2, it is conceivable that a series of reductive dechlorination reactions leading from *p,p'*-DDD and *p,p'*-DDE would result in production of the following metabolites (***p,p'*-DDD**: *p,p'*-DDMS, *p,p'*-DDNS; ***p,p'*-DDE**: *p,p'*-DDMU, *p,p'*-DDNU). All of these compounds have been identified in sediments of the PVS. Transformation of *p,p'*-DDD to *p,p'*-DDMU or *p,p'*-DDMS to *p,p'*-DDNU via dehydrochlorination is theoretically possible. However, this reaction is believed to occur under oxidizing conditions. Subsequent steps indicated in the scheme of Figure S2 (bottom row) involve oxidation, decarboxylation and dehydrogenation reactions. With the exception of *p,p'*-DBP, these products have not been observed as free constituents of the PVS sediments (*1*).
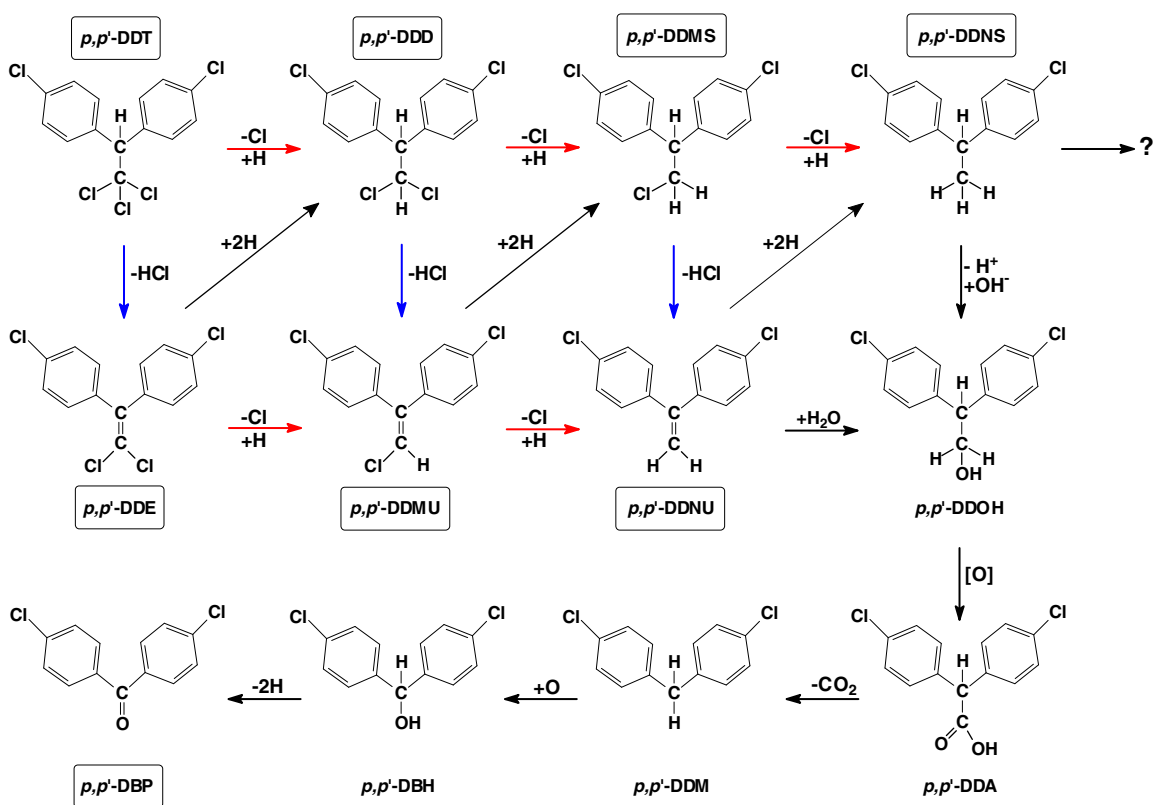
Figure S2: Potential pathways for microbial degradation of DDT. Blue arrows represent dehydrochlorination reactions; red arrows represent reductive dechlorination reactions. Compounds with names shown in boxes have been detected in Palos Verdes Shelf sediments (*1*).

3. PCB Congeners Targeted for Determination

Eighty-four PCB congeners were targeted for determination in sediment samples according to procedures described in detail elsewhere (*1*). Table S1 lists the targeted congeners (in order of elution), EI-NCIMS-identified interferences, and those congeners included in the PCB metrics, ΣPCB_{65} and ΣPCB_{18}.

Table S1: PCB Congeners Determined in Cores 124B1-92 and 124B1-03

Congener #[a]	Known interferences/comments	ΣPCB_{65}[c]	ΣPCB_{18}[d]
1		✓	
2	congener not observed in std.		

Congener #[a]	Known interferences/comments	$\Sigma PCB_{65}{}^c$	$\Sigma PCB_{18}{}^d$
3		✓	
4	tetrachloro-*meta*-xylene (IS)[b]		
9		✓	
6		✓	
8		✓	
19		✓	
18		✓	✓
17		✓	✓
24		✓	
16		✓	
29		✓	
26		✓	✓
25		✓	
31		✓	✓
28		✓	✓
33		✓	
22		✓	
46		✓	
69	PCB 52		
52		✓	✓
49		✓	✓
47		✓	
35		✓	
44		✓	✓
42		✓	✓
41	heptachlor?	✓	
40	elemental sulfur		
100	*o,p'*-DDMU?		
74		✓	✓
70		✓	
66		✓	
91		✓	
60	*p,p'*-DDMU		
92	*p,p'*-DDMU, *o,p'*-DDE		
84	*o,p'*-DDE		
101		✓	
99	*cis*-chlordane?		
119	*trans*-nonachlor?	✓	
83	*p,p'*-DDMS		
97		✓	✓
87		✓	
136	*p,p'*-DDE		

Congener #[a]	Known interferences/comments	ΣPCB$_{65}$[c]	ΣPCB$_{18}$[d]
110	*o,p'*-DDD		
151	unknown brominated compound		
107		✓	
123		✓	
118		✓	
134	*p,p'*-DDD, *cis*-nonachlor?		
114		✓	
153		✓	✓
105		✓	
141		✓	✓
179		✓	
137		✓	
130	*p,p'*-DDT		
138		✓	
158		✓	
129		✓	
187		✓	✓
183		✓	
128 ⌐		✓	
167		✓	
185		✓	
174		✓	✓
177		✓	✓
171 ⌐		✓	
156		✓	
157 ⌐		✓	
201		✓	
172		✓	
180		✓	✓
193		✓	
200		✓	
169		✓	
170	possible coelution w/ PCB 190		
196		✓	✓
189			
195		✓	
194		✓	
205		✓	
206		✓	✓
209		✓	

[a] Congeners numbered according to IUPAC. See ref *2* for congeners 109, 200 and 201. Congeners in bold were supplied by NIST. Non-bolded congeners were obtained from commercial suppliers.

[b] IS=internal quantitation standard.

[c] Congener pairs 128/167, 171/156, and 157/201 were not well resolved and are reported as a single peak for this metric.

[d] Congeners 28 and 31 were quantified separately, but because of poor resolution in core 124B1-92, are reported as a single peak for this metric.

4. Assessment of Potential Reductive Dechlorination of PCBs

Homolog composition: The composition of the PCBs by chlorination level in PVS sediments is shown in Figure S3. Data used for construction of the bar diagrams include only the 68 PCB congeners included in the ΣPCB_{65} metric (Table S1). As indicated by the small error bars, compositions were very uniform throughout both cores, and the homolog distributions were virtually identical in 1992 and 2003. Homolog distributions are also shown for representative Aroclor mixtures based on data of Frame *et al.* (*3*). The PCBs in PVS sediments are dominated by tetra-, penta- and hexachlorobiphenyls with lesser amounts of homologs having fewer than four and more than six chlorines. The compositions are not attributable to a simple mixture of Aroclors (*4*), but the dominance of the tetrachlorobiphenyls is suggestive of the presence of Aroclors 1242 and 1254 (or possibly 1248). The observation of higher chlorinated PCBs including the octachlorobiphenyls and specific congeners not found in Aroclors 1242 and 1254 (*e.g.*, PCBs 195, 196; data not shown), indicates that other Aroclor mixtures, such as 1260 and/or 1262 or 1268, are present.
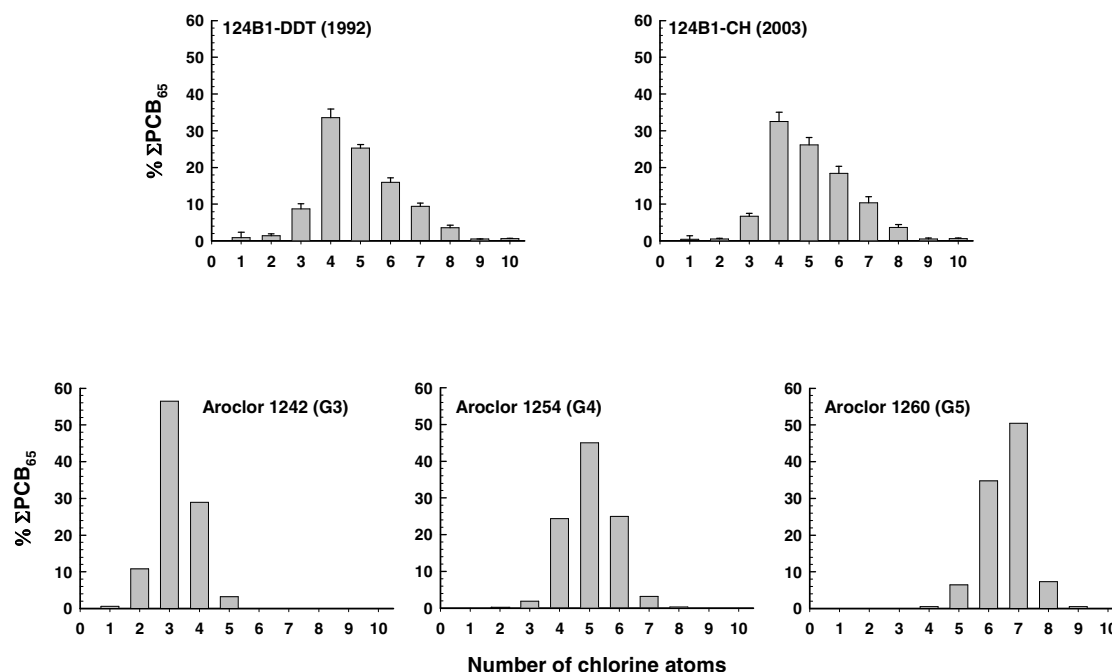
Figure S3: Distribution of PCBs by chlorination level in cores 124B1-92 and 124B1-03 along with distributions found in three common Aroclors (data from ref *3*).

Comparison of vertical concentration profiles of PCBs: Figure S4 shows vertical concentration profiles for ΣPCB_{65}, ΣPCB_{18} and a representative congener, PCB 153, in the 1992 and 2003 cores. For a given core, the three profiles are very similar, and profiles for all PCB metrics are similar between cores. The similarity between profiles for a single core reflects the general uniformity in composition of the PCBs and supports the use of any of the three metrics to track the vertical distribution of PCBs in the sediment column. The similarity of profiles (for a given metric) between cores indicates that there has been no major alteration in the distribution of the PCBs at this site due to mixing and/or degradation between 1992 and 2003. This is reasonable because by 1992, the most heavily contaminated sediments at this location were already buried to depths

greater than 25 cm, significantly below the most intensely bioturbated surficial layers (*5-9*).
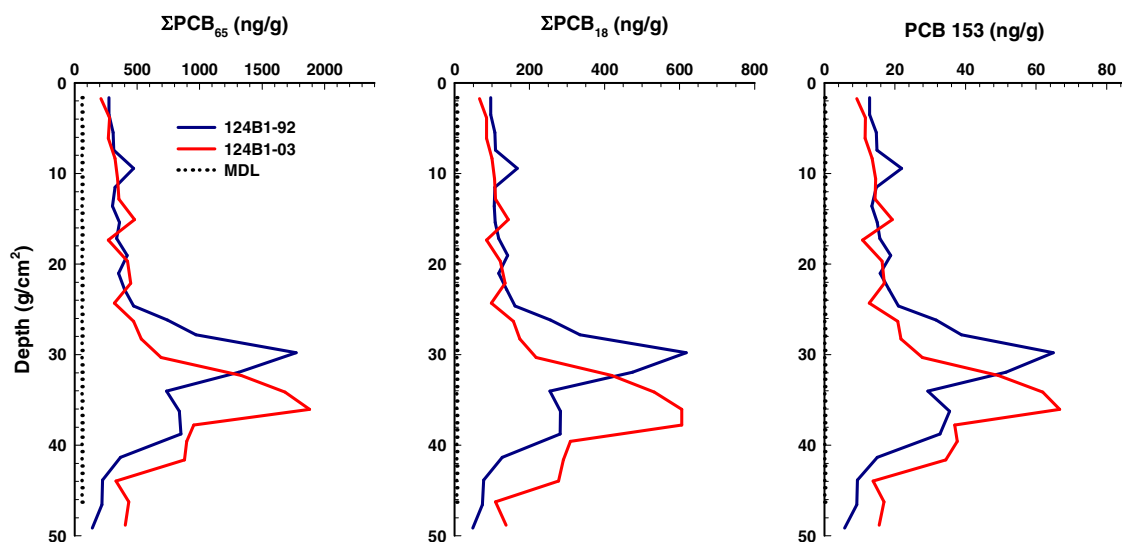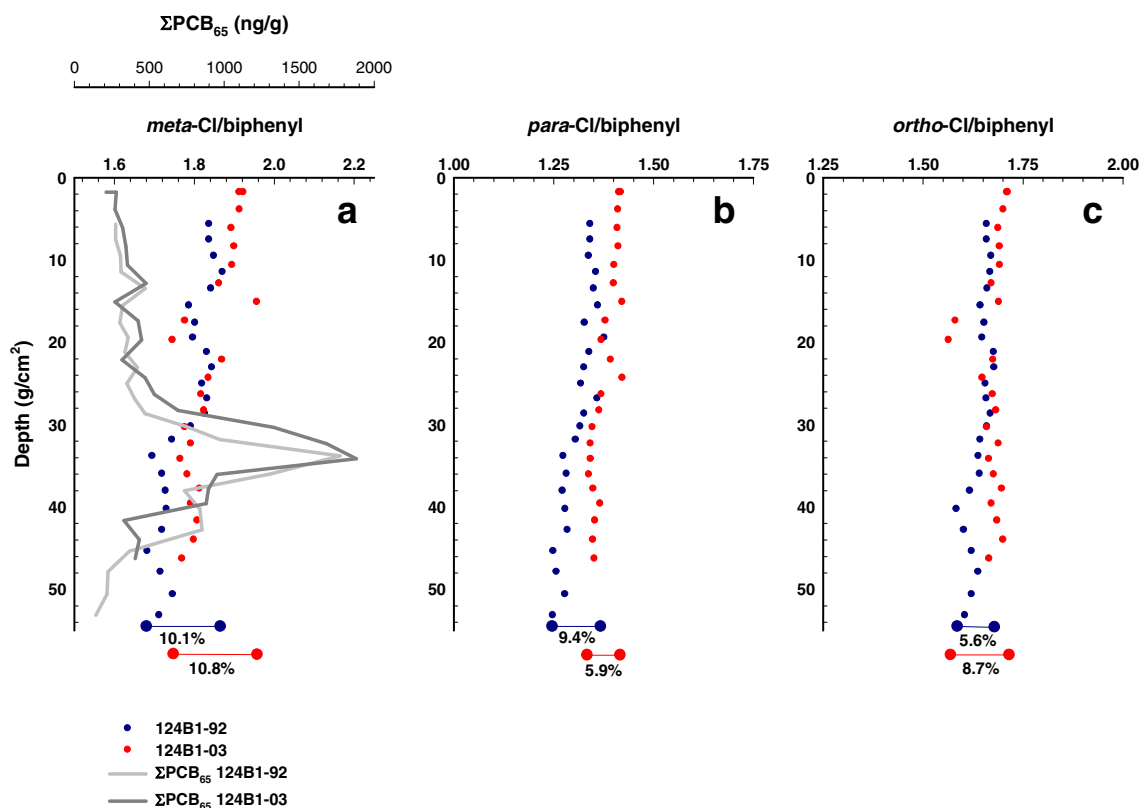

Figure S4: Vertical concentration profiles of PCB congeners in cores collected by the USGS. Core profiles have <u>not</u> been aligned. MDL = method detection limit.

Chlorine substitution patterns: To investigate the hypothesis that the PCBs are being reductively dechlorinated, we examined patterns in the numbers of *ortho-*, *meta-* and *para-*substituted chlorines per biphenyl molecule. Previous field and laboratory studies have shown that microbially mediated reductive dechlorination, operating through at least eight identified 'processes', causes a shift in the distribution of PCBs to lower chlorinated species having a greater proportion of congeners substituted at the *ortho-* position (*10, 11*). This occurs because the microorganisms carrying out the dechlorination reactions generally prefer chlorines attached at the *meta-* and *para-* positions. *Ortho-*dechlorination has rarely been reported (*e.g.*, *12, 13*). For this reason, it is instructive to examine the vertical profiles of *ortho-*, *meta-*, and *para-*substituted chlorines per biphenyl in these sediment cores. The computation of molar abundances of *ortho-*, *meta-*, and *para-*substituted chlorines per biphenyl was carried out as described by Quensen *et al.* (*14*). In

the case of co-eluting congener pairs (*e.g.*, 31/28, 128/167, 171/156, 157/201; see Table S1), equal amounts of the congeners were assumed to be present in each peak, and average numbers of chlorines at *ortho-*, *meta-*, and *para-* positions were computed. One can examine trends in the vertical distribution of chlorine substituent abundance in a given core (that is, evidence of diagenesis; *15, 16*). This depends on the assumption that the composition of PCBs introduced to the sediments is known and/or did not vary significantly over time. The second approach is to compare PCB compositions in cores collected at the same location but at different times (*17, 18*). In the following paragraphs we use both approaches.

Figure S5 shows plots of Cl-substitution abundance and vertical concentration profiles for ΣPCB_{65} in the 124B1 cores. If dechlorination of PCBs had occurred over the period represented by these cores (approximately 40-50 years), one would expect to see a decrease in *meta-* and *para-*chlorine abundances with depth and little or no change in *ortho-*chlorine abundance (*16*). As shown in Figure S5, there is a small but measurable decrease in abundances *ortho-*, *meta-* and *para-*substituted chlorines per biphenyl molecule. The relative percent differences between maximum and minimum chlorine abundances in the 124B1 cores were as follows: **1992 core**-*meta-* (10.1%), *para-* (9.4%), *ortho-* (5.6%), , total (7.0%); **2003 core**-*meta-* (10.8%), *para-* (5.9%), *ortho-* (8.7%), total (7.7%). It is possible that these trends reflect a gradual change in PCB composition, whereby increasing amounts of more heavily chlorinated products were introduced over time. Mixing of surficial sediments throughout this period would serve to smooth any rapid short-term compositional variations of the inputs. Whether the downcore variations seen in Figure S5 are due to compositional changes of PCB inputs over time, reductive

dechlorination or some combination of the two, the rates of change have been exceedingly slow. For example, linear regression analysis of a plot of *meta- + para-* chlorine abundance *versus* estimated age of sediments in core 124B1-92 (based on molecular stratigraphy) yields an 'apparent dechlorination rate' of 0.0078 moles Cl/biphenyl per year ($r^2 = 0.79$). By comparison, Magar *et al*. (*16*) reported an average rate of 0.094 moles Cl/biphenyl per year for ten cores collected from Lake Hartwell, SC.


Figure S5: Vertical profiles of (a) *meta*-Cl/biphenyl abundance and ΣPCB_{65} concentration, (b) *para*-Cl/biphenyl abundance, and (c) *ortho*-Cl/biphenyl abundance in cores 124B1-92 and 124B1-03. Core profiles have been aligned with an offset of 4 g/cm^2. Ranges of isomer abundances are shown below the profiles.

The other feature of note in Figure S5 is the fact that in most cases, chlorine abundances in the 124B1-03 core are similar to or slightly higher than those in coeval layers of the 124B1-92 core. Although the mean difference in total chlorine abundance

between the two cores is small (average relative percent difference = $3.0 \pm 2.4\%$), the generally higher abundances found for the 2003 core are inconsistent with reductive dechlorination during the period 1992-2003. Congener distributions in core sections of equivalent age offer one means of examining this issue in greater detail.

PCB compositions at the depth of maximum concentration (30-32 cm or 29.8 g/cm^2-1992, 34.1 g/cm^2-2003) are shown in Figure S6. Compositional differences are, again, generally quite small (panel c). If reductive dechlorination had taken place in these sediments between 1992 and 2003, one would expect to see significant increases in some lower chlorinated congeners (left side of diagram) with corresponding decreases in abundances of some higher chlorinated congeners (right side of diagram) and an increased proportion of *ortho*-chlorine substituted species. However, no such pattern is observed. In fact, for most congeners, the difference between the cores is exceedingly small and there is no systematic relationship between congeners recognizable as one of the established dechlorination processes. Taken together, the evidence strongly suggests that reductive dechlorination of the PCBs has not occurred to any significant extent on the PVS since at least 1992. This is consistent with the fact that whole-core inventories of ΣPCB_{65}, ΣPCB_{18} and PCB 153 in the 124B1 cores are virtually identical. Based on the distribution of chlorine substituents among congeners as compared with Aroclor compositions, it also seems highly unlikely that reductive dechlorination occurred prior to 1992.
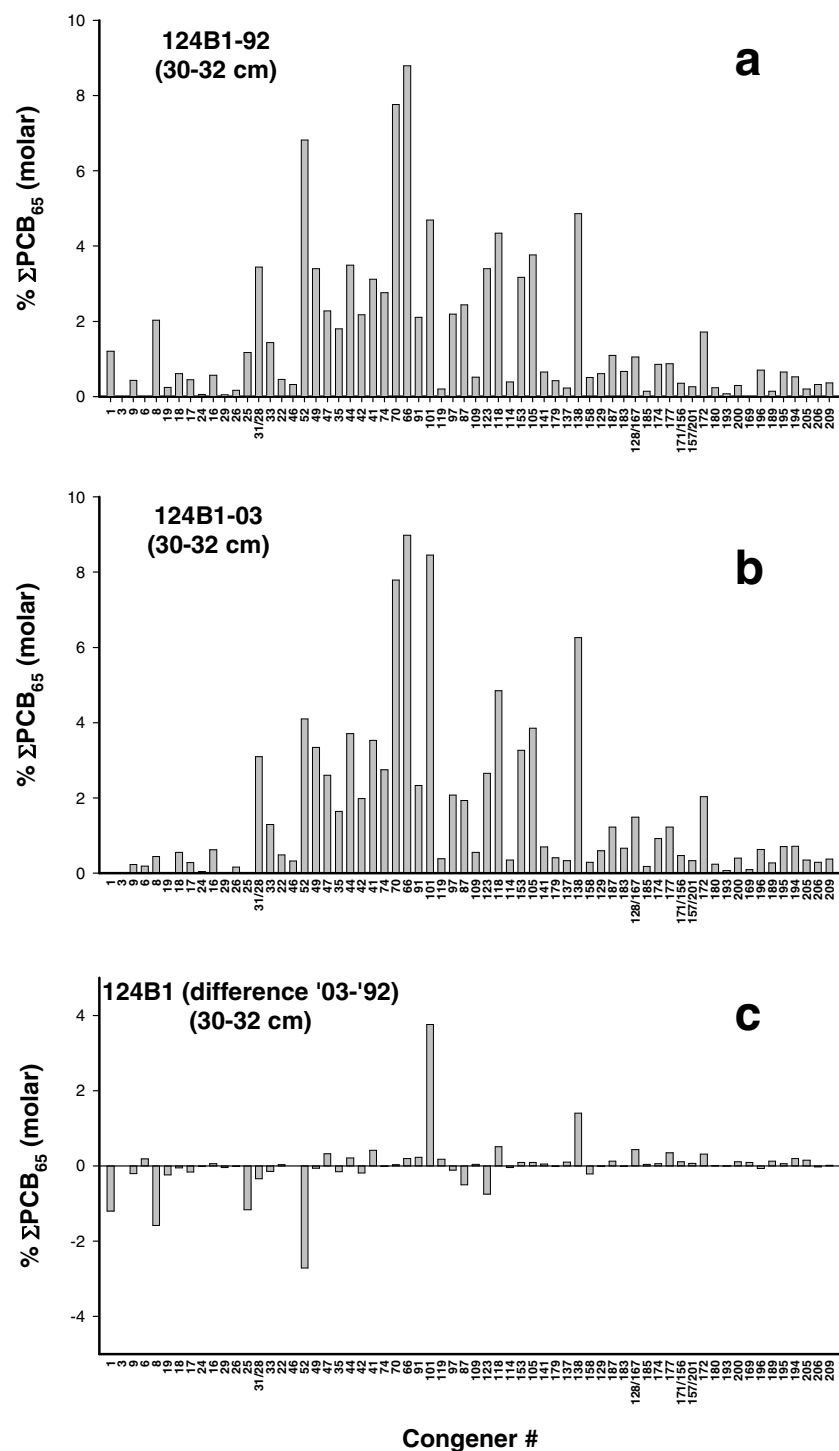
Figure S6: Percent molar composition of PCBs in cores (a) 124B1-92, and (b) 124B1-03 at depths of maximum concentration (30-32 cm) along with (c) plot of difference between cores (2003-1992). Compositions are normalized to ΣPCB_{65}.

5. Core Alignment Procedures

In order to compare chemical inventory data in cores collected from the same location but at different times, we used a statistical core alignment procedure. The purpose of this procedure is to adjust the vertical alignment of two cores so that the corresponding depth intervals are of the same approximate age (coeval). The assumption is that during the period between core collection, intense mixing is constrained to a limited portion of the upper sediment column (perhaps <10 to 20 cm; *7, 8, 19, 20*) and that the vertical concentration/inventory profiles in deeper subsurface sediments have largely been preserved. This requires that diagenetic reactions, which could lead to alteration of the vertical inventory profiles, are negligible.

The alignment procedure consists of three steps: 1) computation of compaction-corrected depths (*1*), 2) calculation of chemical inventories at 1-g/cm^2 depth intervals using linear interpolation, 3) correlation analysis (Pearson, pairwise) of interpolated inventory data with depth offsets varying by increments of 1 g/cm^2. The offset that yields the highest correlation coefficient is taken as the amount of net sediment accumulation in g/cm^2 during the period between core collection. Analysis was carried out using SYSTAT v. 11 software with a range of depth offsets from -20 to +16 g/cm^2 (2003 *vs.* 1992). Data used in the analysis included measured concentrations of *p,p'*-DDE, *p,p'*-DDE + *p,p'*-DDMU, TAB3 (the most persistent of the tetrapropylene-based alkylbenzenes; *4*), PCB 153, and ΣPCB_{65}. TAB3, ΣPCB_{65}, and PCB 153 are conservative geochemical tracers that are unaffected by diagenetic transformation processes at this site. For this reason, direct core-to-core calculations of first-order transformation rates were based on offsets derived from vertical distributions of these compounds.

Figure S7 shows results of the core alignment procedure using data for the 124B1-92 and 124B1-03 cores. Variations among the profiles for a given graph reflect differences in the persistence of the compounds during the time between core collection, and the vertical distribution of these substances as controlled by historical inputs to the sediments.
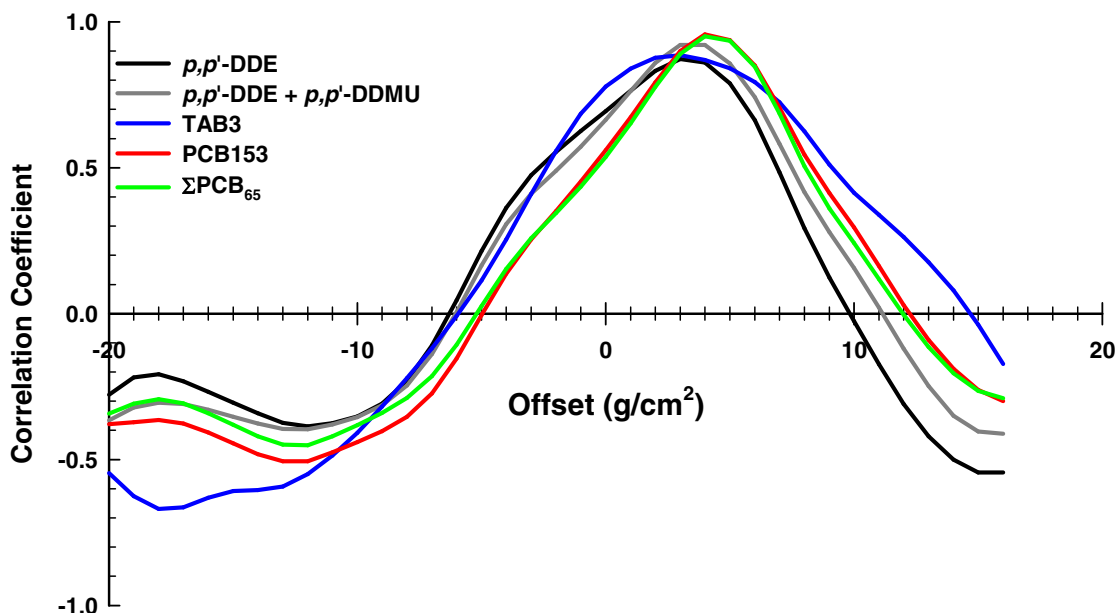
Figure S7: Core alignment curves based on Pearson correlation analyses of inventories *vs*. mass accumulation (g/cm^2) offsets for cores 124B1-92 and 124B1-03.

Figure S8 shows vertical concentration profiles of PCB congener 153 before and after alignment using the optimal offset determined for this compound by the core alignment procedure (4 g/cm^2).
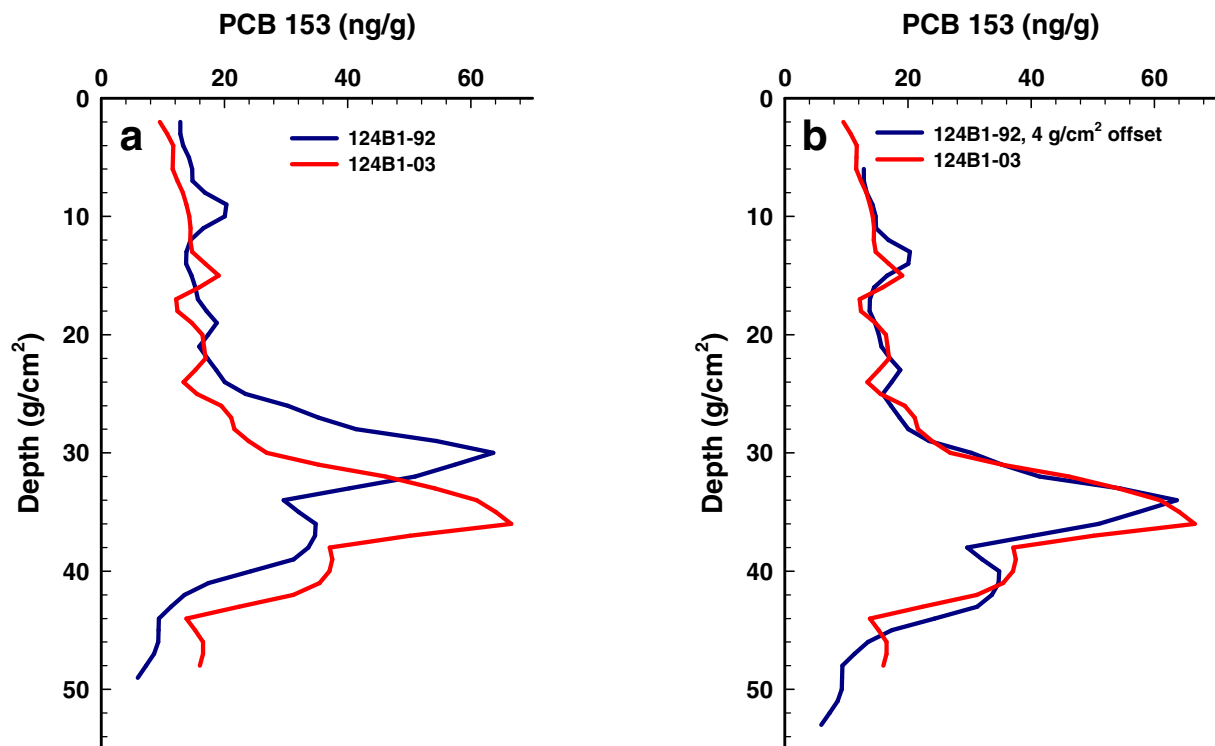
Figure S8: Vertical concentration profiles of PCB 153 (ng/g) in cores 124B1-92 and 124B1-03 cores (a) without depth offset, and (b) with depth offset of 4 g/cm².

6. Transformation Rate Calculations

First-order *p,p'*-DDE transformation rates were calculated using

$$\lambda_{DDE} = \left\{ \ln\left(\frac{[DDE]_{1992}}{[DDE]_{2003}} \right) \right\} / t \qquad (1)$$

where λ_{DDE} is the first-order *p,p'*-DDE transformation rate coefficient (yr^{-1}), $[DDE]_{1992}$ and $[DDE]_{2003}$ are the inventories of *p,p'*-DDE in the 1992 and 2003 cores (μg/cm^2), respectively, and *t* is the time between core collection (yr). Rate constants were determined in two ways: 1) direct comparison of whole-core inventories, and 2) direct comparison of inventories in sediment layers of the same age (*i.e.,* coeval). The latter

was accomplished after statistically aligning vertical concentration profiles of conservative substances (*e.g.*, PCBs, TAB3) in the 1992 and 2003 cores (see section 5).

7. Multi-step Reaction Modeling

Whole-core molar inventories of *p,p'*-DDE, DDMU and DDNU were modeled based on the first-order transformation of : 1) *p,p'*-DDE to *p,p'*-DDMU, 2) *p,p'*-DDMU to *p,p'*-DDNU, and 3) *p,p'*-DDNU to 'products unknown' using the analytical solution derived by Bateman (*21*) for radioactive decay series. The model involves stepwise optimization of the rate coefficients of each reaction such that model predictions match measured inventories (*1*).

8. Mass Balance Calculations for *p,p'*-DDE, *p,p'*-DDMU, *p,p'*-DDNU in the USGS Cores

In this study, *p,p'*-DDE, *p,p'*-DDMU and *p,p'*-DDNU, three putative members of a reductive dechlorination pathway (Figure S2), were measured in two cores. Evidence supporting the assumption that *p,p'*-DDMU is being formed from *p,p'*-DDE and that *p,p'*-DDNU is being formed from *p,p'*-DDMU can be found in changes in the inventories and vertical profiles of these compounds between 1992 and 2003. We were unable to detect any other potential DDT degradation products (beyond *p,p'*-DDNU) in the 2003 core. However, oxidation of the ethylene group of *p,p'*-DDNU would likely lead to formation of *p,p'*-DDA, *p,p'*-DDOH and DBP (*22*). Eganhouse *et al*. (*4*) reported observing significant (but unquantified) amounts of DBP (but not *p,p'*-DDA and *p,p'*-DDOH) in the chlorinated hydrocarbon fraction of the 1992 core, which was analyzed by EC-NCIMS. Our inability to identify DBP in the same fraction of the 2003 core by EI-

HRGC/MS is difficult to explain. P,p'-DDA and p,p'-DDOH, if present, are most likely in a more polar chromatographic fraction, which has not yet been analyzed in either core. It is also possible that these compounds may have become bound to the nonextractable organic matter in the sediments (*23*). In the case of p,p'-DDM and p,p'-DDA this has tentatively been confirmed (*24*). However, alkaline hydrolysis of a pre-extracted sediment sample from the PVS failed to yield detectable concentrations of p,p'-DDT, p,p'-DDE, p,p'-DDMU or p,p'-DDNU.

In order to investigate the p,p'-DDE/p,p'-DDMU/p,p'-DDNU system further, we compared summed molar inventories of these DDT compounds in the 1992 and 2003 cores (Figure S9). The results indicate that at almost all coeval depths, the summed molar inventories of p,p'-DDE, p,p'-DDMU, and p,p'-DDNU in the 1992 core exceed those in the 2003 core (Figure S9a). The difference between summed molar whole-core inventories of the 1992 and 2003 cores was 20.7%. This mass balance deficit is very close to the level of analytical uncertainty (estimated by propagation of error analysis at ~19%), so it is not possible to ascertain whether the deficit is real or not. One possible explanation for this difference is that there are as-yet-unidentified degradation products not included in the mass balance. These products could arise through degradation of any of the three compounds (p,p'-DDE, p,p'-DDMU, p,p'-DDNU) by alternate pathways. Another explanation is incorporation of p,p'-DDE, p,p'-DDMU, or p,p'-DDNU as nonextractable residues in the sedimentary organic matter (*23*). However, as noted above, experiments performed to date show no evidence of this (*24*). The mass balance difference ($\Delta_{\text{mass balance}}$) can be plotted with depth in the aligned cores as shown in Figure S9b. The magnitude of the deficit varies markedly throughout the core, but the profile is

very similar in shape to that of the first-order *p,p'*-DDE transformation rate profile (Figure 3a, main paper). This suggests that the principal contributor to the deficit is the difference between *p,p'*-DDE concentrations, not those of *p,p'*-DDMU or *p,p'*-DDNU, in the two cores. Whether the mass balance deficit is real or not remains unresolved.
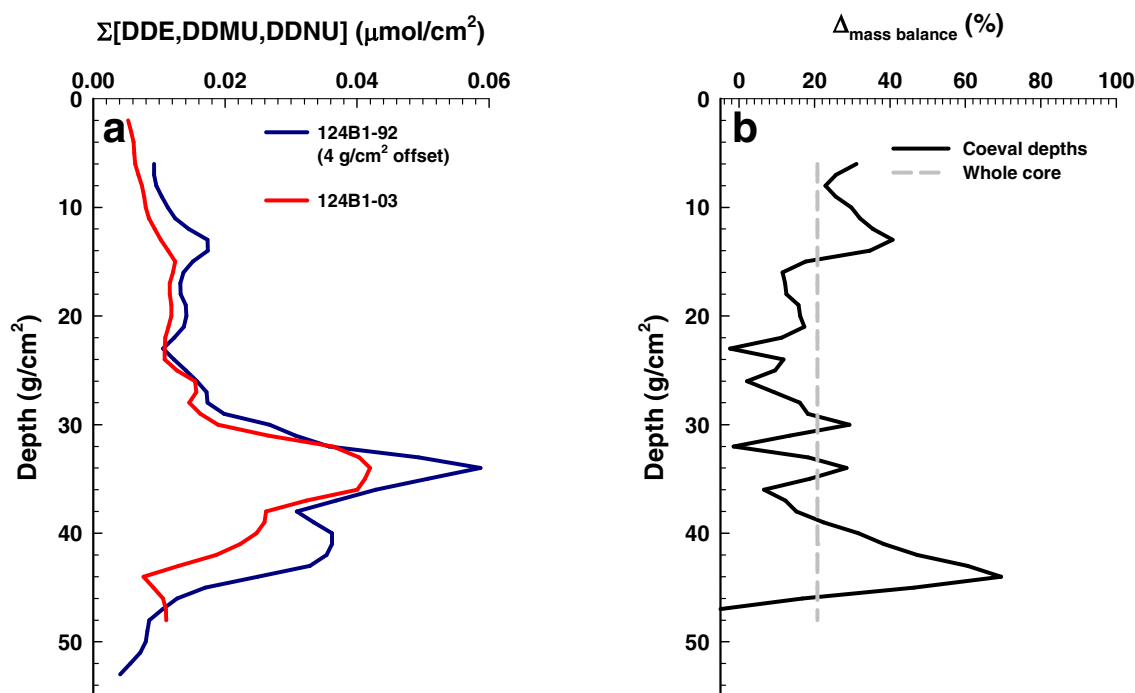
Figure S9. Vertical profiles of (a) summed molar inventories of *p,p'*-DDE, *p,p'*-DDMU, and *p,p'*-DDNU, and (b) percent difference in summed molar inventories of cores 124B1-92 and 124B1-03. Core profiles (panel a) are aligned (4-g/cm² offset).

Literature Cited

(1)   Eganhouse, R.P.; Pontolillo, J. *Assessment of 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (DDE) Transformation Rates on the Palos Verdes Shelf, CA*; U.S. Geological Survey, Reston, VA, Open-File Report, in press.

(2)   Guitart, R.; Puig, P.; Gómez-Catalán, J. Requirement for a standardized nomenclature criterion for PCBs-computer-assisted assignment of correct congener denomination and numbering. *Chemosphere*, **1993,** *27*, 1451-1459.

(3)   Frame, G.M.; Cochran, J.W.; Bøwadt, S.S. Complete PCB congener distributions for 17 Aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resolut. Chromatogr.*, **1996**, *19*, 657-668.

(4)   Eganhouse, R.P.; Pontolillo, J.; Leiker, T.J. Diagenetic fate of organic contaminants on the Palos Verdes Shelf, California. *Mar. Chem.*, **2000**, *70*, 289-315.

(5)   Drake, D.E.; Sherwood, C.R., Wiberg, P.L. *Predictive modeling of the natural recovery of the contaminated effluent-affected sediment, Palos Verdes margin, southern California*; U.S. Department of Justice, Southern California Bight Natural Resource Damage Assessment Expert Reports, 1994.

(6)   Wheatcroft, R.A.; Martin, W.R. *Solid-phase bioturbation processes on the Palos Verdes Shelf*; U.S. Department of Justice, Southern California Bight Natural Resource Damage Assessment Expert Reports, 1994.

(7)   Stull, J.K.; Swift, D.J.P.; Niedoroda, A.W. Contaminant dispersal on the Palos Verdes continental margin-I. Sediments and biota near a major California wastewater discharge. *Sci. Total Environ.*, **1996**, *179*, 73-90.

(8)   Swift, D.J.P.; Stull, J.K.; Niedoroda, A.W.; Reed, C.W.; Wong, G.T.F. Contaminant dispersal on the Palos Verdes continental margin-II. Estimates of the biodiffusion coefficient, D_B, from composition of the benthic infaunal community. *Sci. Total Environ.*, **1996**, *179*, 91-107.

(9)   Lee, H.J.; Sherwood, C.R.; Drake, D.E.; Edwards, B.D.; Wong, F.; Hamer, M. Spatial and temporal distribution of contaminated, effluent-affected sediment on the Palos Verdes margin, southern California. *Cont. Shelf Res.*, **2002**, *22*, 859-880.

(10)   Bedard, D.L.; Quensen, J.F. Microbial reductive dechlorination of polychlorinated biphenyls. In *Microbial transformation and degradation of toxic organic chemicals*; Young, L.Y.; Cerniglia, C.E., Eds.; Wiley-Liss: New York, 1995.

(11)   Wiegel, J.; Wu, Q. Microbial reductive dehalogenation of polychlorinated biphenyls. *FEMS Microbiol. Ecol.*, **2000,** *32*, 1-15.

(12)   Kuipers, B.; Cullen, W.R.; Mohn, W.W. Reductive dechlorination of nonachlorobiphenyls and selected octachlorobiphenyls by microbial enrichment cultures. *Environ. Sci. Technol.*, **1999**, *33*, 3579-3585.

(13)   Palekar, L.D.; Maruya, K.A.; Kostka, J.E.; Wiegel, J. Dehalogenation of 2,6-dibromobiphenyl and 2,3,4,5,6-pentachlorobiphenyl in contaminated estuarine sediment. *Chemosphere*, **2003**, *53*, 593-600.

(14)   Quensen, J.F.; Boyd, S.A.; Tiedje, J.M.; Dechlorination of four commercial polychlorinated biphenyl mixtures (Aroclors) by anaerobic microorganisms from sediments. *Appl. Environ. Microbiol.*, **1990**, *56*, 2360-2369.

(15)   Magar,V.S.; Johnson, G.W.; Brenner, R.C.; Quensen, J.F.; Foote, E.A; Durell, G.; Ickes, J.A; Peven-McCarthy, C. Long-term recovery of PCB-contaminated sediments at the Lake Hartwell Superfund site-PCB dechlorination. 1. End-member characterization. *Environ. Sci. Technol.*, **2005**, *39*, 3538-3547.

(16)   Magar,V.S.; Brenner, R.C.; Johnson, G.W.; Quensen, J.F. Long-term recovery of PCB-contaminated sediments at the Lake Hartwell Superfund site-PCB dechlorination. 2. Rates and extent. *Environ. Sci. Technol.*, **2005**, *39*, 3548-3554.

(17)   Pakdeesusuk, U.; Lee, C.M.; Coates, J.T.; Freedman, D.L. Assessment of natural attenuation via in situ reductive dechlorination of polychlorinated biphenyls in sediments

of the Twelve Mile Creek arm of Lake Hartwell, SC. *Environ. Sci. Technol.*, **2005**, *39*, 954-952.

(18)   Bzdusek, P.A.; Christensen, E.R.; Lee, C.M.; Pakdeesusuk, U.; Freedman, D.L. PCB congeners and dechlorination in sediments of Lake Hartwell, South Carolina, determined from cores collected in 1987 and 1998. *Environ. Sci. Technol.*, **2006**, *40*, 109-119.

(19)   Paulsen, S.C.; List, E.J.; Santschi, P.H. Modeling variability in ^{210}Pb and sediment fluxes near the Whites Point Outfalls, Palos Verdes Shelf, California. *Environ. Sci. Technol.*, **1999**, *33*, 3077-3085.

(20)   Santschi, P.H.; Guo, L.; Asbill, S.; Allison, M.; Kepple, A.B.; Wen, L.-S. Accumulation rates and sources of sediments and organic carbon on the Palos Verdes shelf based on radioisotopic tracers (^{137}Cs, ^{239,240}Pu, ^{210}Pb, ^{234}Th, ^{238}U and ^{14}C). *Mar. Chem.*, **2001**, *73*, 125-152.

(21)   Bateman, H., The solution of a system of differential equations occurring in the theory of radio-active transformations. *Proc. Cambr. Philos. Soc.*, **1910**, *XV*, 423-427.

(22)   Rochkind-Dubinsky, M.L.; Sayler, G.S.; Blackburn, J.W. *Microbiological decomposition of chlorinated aromatic compounds*; Marcel Dekker, New York, 1987.

(23)   Schwarzbauer, J.; Ricking, M.; Littke, R. DDT-related compounds bound to the nonextractable particulate matter in sediments of the Teltow Canal, Germany. *Environ. Sci. Technol.*, **2003**, *37*, 488-495.

(24)   Schwarzbauer, J., Rheinisch-Westfälische Technische Hochschule Aachen, and M. Ricking, Free University of Berlin, unpublished results.