

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

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From 1947 to 1971 the world's largest manufacturer of DDT discharged process wastes into the sewers of Los Angeles County. Roughly 870–1450 t of DDT were released to the ocean off Palos Verdes, CA, a portion of which (~100 t) resides in sediments on the continental shelf and slope. The most abundant DDT compound in the sediments, *p,p'*-DDE, is degrading by reductive dechlorination, but the rate of transformation and factors controlling it are not well understood. In order to estimate *in situ* transformation rates and predict the long-term fate of *p,p'*-DDE, box cores were collected in 1992 and 2003 from a single location on the Palos Verdes Shelf and analyzed for 8 DDT compounds and 84 polychlorinated biphenyl (PCB) congeners. The PCBs show no evidence of dechlorination, and inventories did not change between 1992 and 2003. By contrast, the inventory of *p,p'*-DDE decreased by 43%, whereas that of *p,p'*-DDMU, the putative reductive dechlorination product, increased by 34%. The first-order transformation rate for *p,p'*-DDE at the study site is $0.051 \pm 0.006 \text{ yr}^{-1}$. A multistep reaction model suggests that inventories of *p,p'*-DDE and *p,p'*-DDMU will continue to decline, whereas that of *p,p'*-DDNU will reach a maximum around 2014.

Introduction

In 1947 the world's largest producer of technical DDT, Montrose Chemical Corporation, began discharging process wastes into sewers of the Los Angeles County Sanitation Districts (LACSD). By 1971, when inputs were terminated, Montrose had introduced ~1500–2500 t of DDT to LACSD's municipal wastewater treatment plant in Carson, CA. Roughly 58% this amount (870–1450 t) was released to ocean waters off Palos Verdes Peninsula through a submarine outfall system at White Point (Figure S1a, Supporting Information), resulting in the accumulation of highly contaminated marine sediments on the continental shelf and slope. The uptake of DDT and its transformation products from Palos Verdes Shelf (PVS) sediments by indigenous marine life has been known since the early 1970s (1), but it was the dramatic reproductive failure of the brown pelican off southern California (2) and the demise of the bald eagle from the Channel Islands (3) that spurred concerns over the broader effects of DDT on the marine ecosystem.

In June 1990, a lawsuit was filed by the National Oceanic and Atmospheric Administration (NOAA) under the natural resource damages provision of CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act). A large multidisciplinary investigation of the PVS was subsequently undertaken by scientists from the U.S. Geological Survey (USGS) and other research institutions in the early 1990s, results of which can be found elsewhere (4–7). In 1992, it was determined that 109 t of total DDT (total DDT = *p,p'*- and *o,p'*- isomers of DDT, DDD, and DDE + *p,p'*-DDMU) and more than 66 t of *p,p'*-DDE were present within a relatively thin (<60 cm) sedimentary deposit on the shelf and slope adjacent to and downcurrent from the wastewater outfalls (8, 9). In August 1997 the PVS was added to the National Priorities List by the U.S. Environmental Protection Agency (USEPA).

The fate of DDT and its transformation products in PVS sediments and their potential mobilization have been the subject of study for nearly forty years (e.g., refs 4, 10, 11). At issue is whether the most highly contaminated layers of sediment, presently at sub-bottom depths of 20–45 cm, will be re-exposed and mobilized or if continued burial and biotransformation can prevent this from happening. Models have been developed in an effort to predict the long-term behavior of the deposit (12, 13). An important but poorly constrained component of these models is the rate of transformation of *p,p'*-DDE, a potent androgen antagonist (14), which constitutes ~65% of the total DDT (5).

For many years *p,p'*-DDE was considered a highly persistent chemical (15, 16). Field data obtained by the USGS in 1992, however, showed that *p,p'*-DDMU, a potential reductive dechlorination product of *p,p'*-DDE (17), was ubiquitous in PVS sediments (18). Microcosm experiments conducted with sediments from the PVS in the late 1990s demonstrated unequivocally that *p,p'*-DDE could be reductively dechlorinated by native microorganisms (19–21). These experiments also showed that rates of dechlorination in PVS sediments increased with distance downcurrent from (to the northwest of) the outfalls. This spatial pattern is consistent with field data on the relative abundance of *p,p'*-DDMU (22), but the factors controlling rates of dechlorination on the shelf are poorly understood.

In 2005, as part of their biennial benthic survey, the LACSD collected sediment cores on the PVS for chemical analysis. For the first time, the list of analytes included *p,p'*-DDMU. Results obtained by the LACSD suggested that rates of dechlorination had changed since the early 1990s (5). The PVS is presently under investigation by the USEPA as part of an effort to remediate the site, one option for which is monitored natural attenuation (23). Therefore, a project was initiated to provide a better understanding of the range of reductive dechlorination rates on the PVS and the environmental factors that control them. The objectives of the present study were to (1) determine *in situ* transformation rates of *p,p'*-DDE at a location ~7 km downcurrent from the LACSD outfalls (Figure S1), (2) compare these rates with existing field and laboratory (microcosm) data, and (3) predict the long-term fate of *p,p'*-DDE and its principal transformation products at the study site.

Materials and Methods

Sample Collection. Sediment cores were collected by the USGS and the LACSD; details of the navigation, collection, and handling procedures can be found elsewhere (22). The USGS collected box cores on the PVS in July 1992 (24). One of these cores, designated 124B1, was obtained on July 6

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approximately 7 km downcurrent from the outfall system (33°43'50.2" N, 118°24'4.7" W; Figure S1b); a subcore, hereafter referred to as 124B1-92, was taken from the box for chemical analysis. On July 29, 2003, a second box core was collected by the USGS from the same approximate location (33°43'49.6" N, 118°24'5.2" W; Figure S1b) using identical procedures; a subcore, hereafter referred to as 124B1-03, was obtained from this box core. The 1992 and 2003 cores were collected 11.1 years apart, approximately 22 ± 5 m from each other.

The LACSD has conducted biennial surveys of the benthic environment off Palos Verdes since 1981 (9). In this paper we report analytical chemistry results obtained by the LACSD for gravity cores collected in July 1991 and June 2005 at two locations along the 60-m isobath (stations 3C, 6C; Figure S1a). Station 3C (33°43'50.4" N, 118°24'7.8" W) is near the site where the USGS cores were collected (Figure S1b).

Sample Preparation. The methods used for preparation of the 1992 and 2003 USGS cores were identical and have been described previously (5, 22); only a brief summary is given here. Sediments were thawed, homogenized, and spiked with recovery surrogates prior to Soxhlet extraction. Extracts were concentrated by rotary evaporation and treated for removal of water and elemental sulfur. A fraction containing the chlorinated hydrocarbons (DDTs, PCBs) and the long-chain alkylbenzenes (LCABs) was isolated by adsorption chromatography. This fraction was split for separate analyses of the DDTs, PCBs (and LCABs; (25)). Procedures used by the LACSD to prepare samples for determination of *p,p'*-DDE and *p,p'*-DDMU are given elsewhere (26).

Instrumental Analysis and Data. Details of the procedures used for instrumental analysis of fractions containing the chlorinated hydrocarbons (USGS cores) are available separately (5, 22). Briefly, 8 DDT compounds (*p,p'*- and *o,p'*-DDT, DDD, and DDE plus *p,p'*-DDMU, and DDNU) and 84 PCB congeners were determined by high-resolution gas chromatography/electron capture detection (HRGC/ECD) with confirmation by HRGC/electron impact mass spectrometry and electron capture-negative chemical ionization mass spectrometry (EC-NCIMS). To illustrate the behavior of the PCBs, two metrics are used in this paper. ΣPCB_{65} refers to the summed concentrations of 65 PCB peaks (62 separated + 3 pairs of coeluting congeners) free of major interference. ΣPCB_{18} is the summed concentration of 18 major PCB peaks (19 congeners) spanning a wide range of chlorination; no evidence of interference exists for these congeners. The identities of the PCB congeners included in these metrics are provided in Table S1. The LACSD measured *p,p'*-DDE and *p,p'*-DDMU using HRGC/MS (26).

Quality Assurance/Quality Control. In the case of USGS core analyses, quality assurance guidelines were developed as part of the Montrose investigations (27). Detailed information on method performance for the chlorinated hydrocarbon analyses (USGS sediment cores) can be found elsewhere (5, 22). For purposes of this comparative study, a NIST (National Institute of Standards and Technology) standard reference material (1941a) was used to assess the accuracy of the measurements. Concentrations of *p,p'*-DDE determined in SRM 1941a were 6.57 ± 0.78 ng/g ($n = 4$) versus a certified concentration of 6.59 ± 0.56 ng/g (28). Procedures for quality assurance/quality control used in the LACSD core analyses can be found elsewhere (26).

Results and Discussion

Field Evidence for Reductive Dechlorination of *p,p'*-DDE. The ubiquitous presence of *p,p'*-DDMU in shelf sediments, first observed in 1992 (18), cannot by itself be taken as evidence that reductive dechlorination of *p,p'*-DDE is occurring on the PVS. This is because it is not known whether

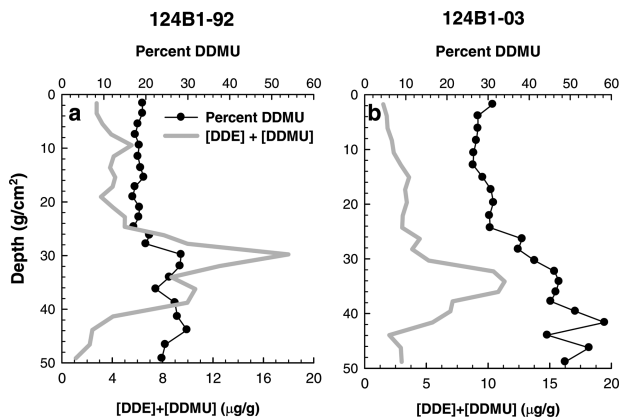


FIGURE 1. Percent *p,p'*-DDMU (relative to the sum, *p,p'*-DDE + *p,p'*-DDMU) and vertical concentration (*p,p'*-DDE + *p,p'*-DDMU) profiles in cores collected by the USGS in (a) 1992 (124B1-92) and (b) 2003 (124B1-03). Uncertainty in percent *p,p'*-DDMU is estimated at 18.6% (rsd). See Figure S1 for sampling locations.

p,p'-DDMU was originally present in the wastewater effluent particles that were discharged through the outfall system and delivered to PVS sediments (5). It is also possible that dehydrohalogenation of *p,p'*-DDD during the early stages of sedimentation may have contributed some of the *p,p'*-DDMU found in PVS sediments, but this hypothesis cannot be tested with available data. The relative abundance of the DDDs was constant between 1972 and 1992 (5) suggesting that dehydrohalogenation of DDD was insignificant during this period. Shelf sediments along the 60-m isobath are reducing below the upper few cm of the sediment–water interface (29), so redox conditions within the sediment column should be conducive to reductive dechlorination.

Several lines of evidence support the hypothesis that reductive dechlorination of *p,p'*-DDE is occurring under field conditions on the PVS. First, microcosm experiments demonstrated that when PVS sediments were amended with ^{14}C -labeled DDE, *p,p'*-DDMU was produced (19); ^{14}C -mass balances at the end of the experiments were 85–93%, and *p,p'*-DDE and *p,p'*-DDMU accounted for $\geq 99\%$ of the recovered radioactivity. At the same time, autoclaved controls showed no *p,p'*-DDMU production, and sediments spiked with ^{14}C -labeled *p,p'*-DDD yielded only trace amounts of *p,p'*-DDMU. These results indicate that not only are the *in situ* geochemical conditions favorable to reductive dechlorination of *p,p'*-DDE, but microorganisms resident in PVS sediments can carry out the transformation. Considering the results of the microcosm experiments and the fact that production of *p,p'*-DDMU from *p,p'*-DDD (via dehydrochlorination; Figure S2) would likely require oxidizing conditions (30), it seems reasonable to assume a precursor–product relationship between *p,p'*-DDE and *p,p'*-DDMU.

A second line of evidence is the vertical distribution of the percent *p,p'*-DDMU in sediment cores. Figure 1 shows plots of the percent *p,p'*-DDMU and summed concentrations of *p,p'*-DDE and *p,p'*-DDMU in the 1992 and 2003 USGS cores. In 1992, percent *p,p'*-DDMU was fairly constant (~20%) in the upper 25 g/cm² of the sediment column. At depths greater than ~25 g/cm² there was an apparent increase suggesting that reductive dechlorination was occurring, but the trend was not strong. Data for the 2003 core show higher abundances of *p,p'*-DDMU in the upper ~25 g/cm² (about 30–35%) with a marked increase in percent *p,p'*-DDMU at depths greater than ~25 g/cm². These trends suggest that diagenetic transformation of *p,p'*-DDE to *p,p'*-DDMU is occurring and that significant changes in the relative abundances of *p,p'*-DDE and *p,p'*-DDMU took place between 1992 and 2003. This assumes that the differences between

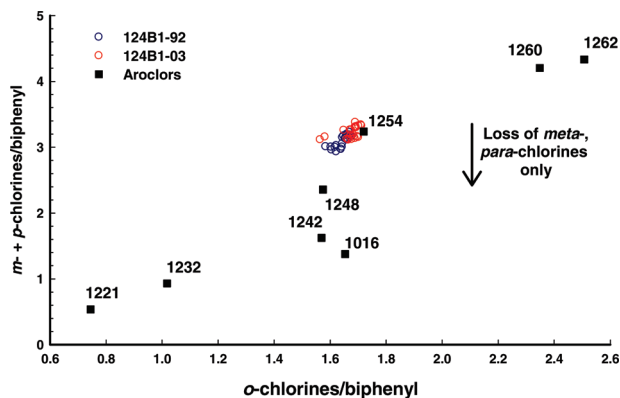


FIGURE 2. Plot of average [*meta*- + *para*-chlorine] abundance versus *ortho*-chlorine abundance in the 124B1 cores and in Aroclors based on 68 PCB congeners (33).

core profiles are not due to spatial variations in DDT composition.

To address this concern, we evaluated the composition and inventories of the PCBs, a class of wastewater-derived compounds believed to be recalcitrant in sediments of the PVS. By analyzing the 1992 and 2003 cores using the same techniques and for the same PCB congeners, we were able to examine both the vertical variation in composition of the PCBs and changes in composition over time (i.e., between cores). Reductive dechlorination results in a shift in the distribution of PCBs from higher to lower chlorinated species with a greater proportion of congeners substituted at the *ortho*- position (31, 32). PCB compositions in the 1992 and 2003 cores were nearly uniform with depth and were dominated by tetra-, penta-, and hexachlorobiphenyls (Figure S3); only a small enrichment in lower chlorinated species was found with depth (22). Examination of the abundances of *meta*- and *para*-substituted chlorines per biphenyl reveals a small decrease with depth in both cores (6–11%; Figure S5). However, there is no apparent enrichment of *ortho*-substituted PCBs with depth or between cores. In fact, there is slightly greater total chlorine abundance in the 2003 core compared with the 1992 core (4.89 vs 4.74 Cl/biphenyl, respectively; (22)).

These results are summarized in Figure 2, which shows a plot of [*meta*- + *para*-] versus *ortho*-chlorine abundances for the 68 congeners free of major interference in the USGS cores along with corresponding data for some common Aroclors (33). Assuming that the original sources of PCBs to PVS sediments had chlorine substituent compositions similar to the Aroclors shown here, preferential dechlorination at *meta*- and/or *para*-chlorine positions would be expected to result in compositions plotting below the respective Aroclor data points, as indicated by the downward facing arrow (cf ref (34)). For mixed Aroclor inputs (5, 22), dechlorinated PCB compositions would plot below the relevant Aroclor mixing lines. Instead, the USGS core data fall within very narrow ranges near but slightly to the left of the datum for Aroclor 1254. These results strongly suggest that reductive dechlorination of the PCBs is *not* occurring at the study site and that differences in *p,p'*-DDMU abundance between the 1992 and 2003 cores are not attributable to spatial heterogeneity.

Another line of evidence for reductive dechlorination of *p,p'*-DDE is the observed decrease in whole-core inventories of this compound between 1992 and 2003 and the concomitant increase in the inventory of *p,p'*-DDMU (Table 1). These changes could be ascribed to spatial heterogeneity unless it can be shown that other chemically similar wastewater-derived constituents in the sediments are conserved. Differences between the whole-core molar inventories of ΣPCB_{65} , ΣPCB_{18} , and a representative PCB congener (#153)

in the 1992 and 2003 cores range from 3.3 to 11% (Table 1). Uncertainty for these metrics, based on replicate ($n = 5$) analyses of PVS sediments, is estimated at 9.2–11% (relative standard deviation). Thus, the PCBs are conserved. This conclusion is consistent with evidence discussed above that PCB compositions in these sediments are remarkably uniform and do not show evidence of reductive dechlorination. The same conservative behavior was found in PVS sediments for the tetrapropylene-based alkylbenzenes (TABs), a class of surfactant chemicals known to be highly persistent in anoxic sediments (25). Because the PCBs and TABs are conservative, their vertical concentration profiles can be used to align the 1992 and 2003 cores so that chemical inventories in coeval sediment layers can be directly compared (Supporting Information, section 5). More importantly, the physicochemical properties of the PCBs and TABs span those of *p,p'*-DDE (35–37). Consequently, any decrease in the inventory of *p,p'*-DDE between the 1992 and 2003 cores must be caused by *in situ* transformation, not physical transport (e.g., mixing, porewater advection, diffusion, sorption/desorption), processes. As shown in Table 1, the whole-core inventory of *p,p'*-DDE in the 2003 core was 43.2% less than it was in the 1992 core, whereas whole-core inventories of *p,p'*-DDMU and *p,p'*-DDNU (presumed reductive dechlorination product of *p,p'*-DDMU; Figure S2) increased by 33.5% and 32.9%, respectively. Together, these data provide compelling evidence that reductive dechlorination of *p,p'*-DDE (and possibly *p,p'*-DDMU) is occurring in PVS sediments.

***p,p'*-DDE Transformation Rates.** First-order transformation rates for *p,p'*-DDE were calculated from whole-core inventories and by direct comparison of inventories in coeval layers of the 1992 and 2003 cores (Table 2; Supporting Information, section 6). The rate obtained from whole-core inventories in the USGS cores was $0.051 \pm 0.006 \text{ yr}^{-1}$ (mean $\pm 1 \text{ sd}$). Mean and median rates obtained by direct comparison of coeval layers were $0.052 \pm 0.025 \text{ yr}^{-1}$ and $0.045 \pm 0.025 \text{ yr}^{-1}$, respectively (Figure 3). Whole-core inventories of *p,p'*-DDE were also computed for the 1991 (1 core/station) and 2005 (3 cores/station) cores collected by the LACSD. The following rates were obtained: station 3C-0.085, 0.058, and 0.047 yr^{-1} (mean $\pm 1 \text{ sd}$: $0.064 \pm 0.020 \text{ yr}^{-1}$); station 6C-0.018, 0.028, and 0.013 yr^{-1} (mean $\pm 1 \text{ sd}$: $0.020 \pm 0.007 \text{ yr}^{-1}$).

The transformation rate at LACSD station 3C ($0.064 \pm 0.020 \text{ yr}^{-1}$) is similar to but somewhat higher and more variable than the rate obtained from the USGS core data ($0.051 \pm 0.006 \text{ yr}^{-1}$), but the uncertainties overlap. The LACSD cores span a longer period of time, and it is also possible that environmental conditions at the two locations are not the same. A significant amount of spatial variability exists on the PVS (6) and this may have contributed to the spread of values. Considering these factors, rates obtained from LACSD and USGS core data agree remarkably well.

Figure 3a shows a vertical profile of the first-order transformation rate coefficient for *p,p'*-DDE (λ'_{92-03}) as a function of depth calculated from *p,p'*-DDE inventories in the aligned USGS cores. In general, rates are somewhat lower at shallower depths (6–28 g/cm²) and tend to increase irregularly with depth to about 44 g/cm², after which a rapid decrease occurs. The aligned vertical concentration profiles in Figure 3b and c provide a means of visualizing what the concentrations of parent (*p,p'*-DDE) and product (*p,p'*-DDMU) were at coeval depths in the two cores. In the most heavily contaminated layers (about 30–45 g/cm²), rates are somewhat variable; highest rates are found on the lower shoulder of the subsurface peak.

The *p,p'*-DDE transformation rates derived from field data can be compared to rates obtained in laboratory microcosm studies. A detailed description of these experiments and their relevance to the present study can be found elsewhere (22).

TABLE 1. Whole-Core Molar Inventories of DDT Compounds and PCBs in Cores Collected by the USGS in 1992 and 2003

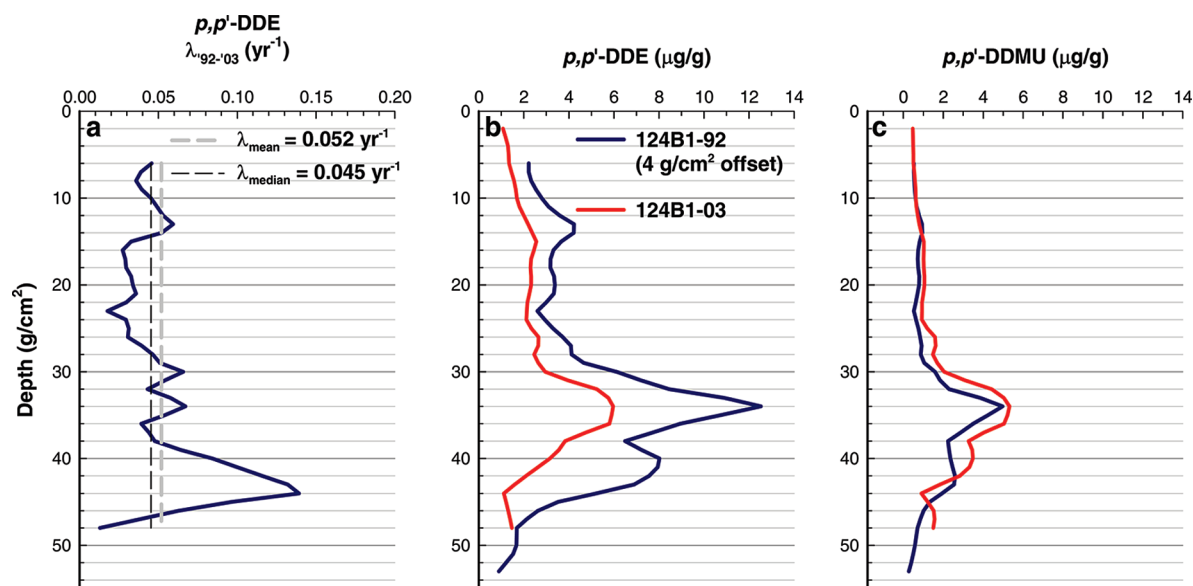
core	<i>p,p'</i> -DDE ($\mu\text{mol}/\text{cm}^2$)	<i>p,p'</i> -DDMU ($\mu\text{mol}/\text{cm}^2$)	<i>p,p'</i> -DDNU ($\mu\text{mol}/\text{cm}^2$)	ΣPCB_{65} (nmol/ cm^2)	ΣPCB_{18} (nmol/ cm^2)	PCB 153 (nmol/ cm^2)
124B1-92	0.681	0.229	0.0546	81.6	26.8	2.98
124B1-03	0.387	0.306	0.0725	90.2	27.6	1.13
RPD (%) ^a	-43.2	33.5	32.9	10.6	3.3	5.3

^a RPD (relative percent difference) = [(inventory₁₉₉₂ - inventory₂₀₀₃)/inventory₁₉₉₂] × 100.

TABLE 2. First-Order *p,p'*-DDE Transformation Rates in Sediments of the Palos Verdes Shelf with Results of Relevant Microcosm Studies (Based on Whole-core Inventories)

station/core ^a	year(s) of study	investigation	comments	transformation rate (yr^{-1})	half-life (yr)
124B1-92, -03	1992–2003	this study	field study	0.051 ± 0.006	13.6 ± 1.7
3C	1991–2005	LACSD	field study	0.064 ± 0.020	10.8 ± 3.4
6C	1991–2005	LACSD	field study	0.020 ± 0.007	34.7 ± 12.1
3C	^b	Quensen et al.(20)	microcosm, 10 °C	0.073	9.5
3C	^b	Quensen et al.(20)	microcosm, 15 °C	0.151	4.6
3C	1997	Deming and Carpenter(21)	microcosm, 30–40 cm, 12 °C	0.23	3.0
6C	1997	Deming and Carpenter(21)	microcosm, 2–30 cm, 12 °C	0.087	8.0
8C	1997	Deming and Carpenter(21)	microcosm, 2–30 cm, 12 °C	0.069	10

^a See Figure S1 for station/core locations. ^b Not reported.

**FIGURE 3. Vertical profiles of (a) first-order *p,p'*-DDE transformation rate constant, λ_{92-03} , computed from aligned core data, and concentrations of (b) *p,p'*-DDE, and (c) *p,p'*-DDMU in 1992 and 2003 cores. Core profiles are aligned (4-g/ cm^2 offset). Uncertainty in estimated first-order *p,p'*-DDE transformation rate constants is 0.025 yr^{-1} .**

Briefly, box cores were obtained from locations along the 60-m isobath on the PVS (stations 3C, 5C, 6C, 8C; Figure S1a). Sediment samples were either collected from the surface of the cores or from discrete sub-bottom depths and placed inside chambers where they were spiked with ¹⁴C-labeled *p,p'*-DDE (19–21). The microcosms were kept sealed, and preliminary aging of the *p,p'*-DDE-spiked sediments was not possible. Some of the experiments were conducted near or at the *in situ* temperature of PVS sediment (~12 °C), whereas others were not. Increased *p,p'*-DDE dechlorination rates were observed in sediments collected at greater distance from (i.e., to the northwest of) the outfalls. This pattern is consistent with a trend of increasing relative abundance of *p,p'*-DDMU to the northwest along the 60-m isobath (22) and the higher transformation rates calculated for sediments collected near LACSD station 3C than those for sediments from station 6C (Table 2). A major finding of the microcosm studies of Quensen et al. (19, 20) was that methanogenic conditions

favored higher rates of dechlorination (~4×) than sulfidogenic conditions.

Table 2 compares first-order *p,p'*-DDE transformation rates obtained from microcosm experiments that best approximated field conditions with rates derived from USGS and LACSD field data. For a given location, and accounting for slight deviations from *in situ* sediment temperature, the field-derived rates are lower than, by factors of ~2–4, those obtained in the most comparable microcosm experiments. This is attributable to at least two factors. First, the bioavailability of *p,p'*-DDE may have been greater in the microcosm experiments than it is in the field. Laboratory studies have shown that aging of sediments spiked with hydrophobic organic chemicals (HOCs), such as *p,p'*-DDE, causes a decrease in bioavailability (see references in (38)). This is due to the fact that HOCs become less accessible to microorganisms capable of metabolizing them through binding to or within highly sorptive phases (e.g., kerogen,

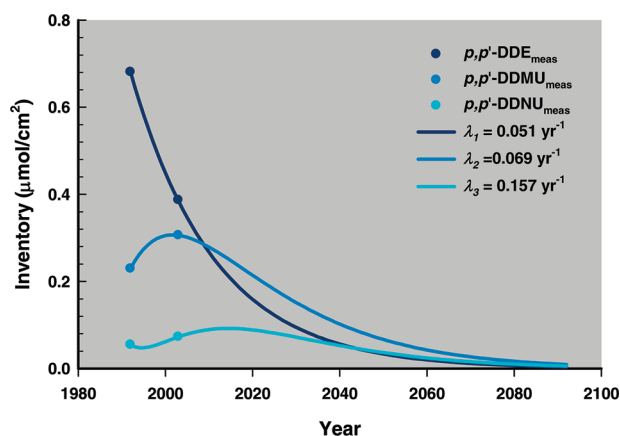


FIGURE 4. Trajectories of p,p' -DDE, p,p' -DDMU, and p,p' -DDNU molar inventories near station 3C predicted from multistep reaction model, 1992 to 2092. Solid symbols are the measured whole-core molar inventories for cores collected in 1992 and 2003.

oil, black carbon) that are present in the sedimentary organic matter (39). These phases are known to exist in PVS sediments (40–42). Second, the microcosms did not have a continuing supply of sulfate, and this electron acceptor may (and in some cases is known to) have been exhausted in the microcosms during the period of incubation with the result that methanogenic conditions developed. Quensen et al. (20) observed sulfate at all depths in the cores at the time of collection, indicating that sulfate was available within the sediment column under field conditions. Van Cappellen and Santschi (29) obtained porewater-chemistry profiles for cores collected at stations 6C and 8C in 1997. At station 6C they showed only a moderate decrease in sulfate concentration (from 30 to 28 mM), mostly occurring within the upper 5 cm of the sediment column, down to a depth of 20 cm. Reactive transport modeling of the porewater data showed that sulfate reduction was the dominant terminal electron-accepting process within PVS sediments. Because rates of dechlorination under methanogenic conditions are four times greater than those under sulfidogenic conditions, rates obtained in some of the microcosm experiments may not have been characteristic of those in the field where sulfate is readily available.

Long-term Fate of p,p' -DDE, p,p' -DDMU, and p,p' -DDNU. Predicting the long-term fate of p,p' -DDE on the PVS requires consideration of many processes (12, 13). However, if one assumes that reductive dechlorination is the dominant pathway leading from p,p' -DDE to p,p' -DDMU and that p,p' -DDMU is further degraded to as-yet-identified products (Figure S2), it is possible to model the time course of this transformation as a series of first-order decays. The equations provided by Bateman (43) were applied to this problem (Supporting Information, section 7). The main assumptions in the model are the following: (1) all reactions proceed by first-order kinetics, (2) no competing reactions are involved, (3) reaction rates do not change over time, and (4) no other processes are responsible for losses of these compounds from the sediments.

Figure 4 shows trajectories of p,p' -DDE, p,p' -DDMU, and p,p' -DDNU molar inventories near station 3C predicted from the multistep reaction model for the period between collection of the 124B1 cores (1992–2003) and projected forward by 100 years. As reductive dechlorination proceeds, there is an increase in the inventory of p,p' -DDMU until 2002, after which inventories of this compound decline as the rate of p,p' -DDMU production exceeds the rate of p,p' -DDMU supply. According to this model scenario, p,p' -DDMU inventories peak in about 2014 and decline thereafter; half-

lives for p,p' -DDE, p,p' -DDMU, and p,p' -DDNU are 13.6, 10.0, and 4.4 years, respectively.

How do these predictions relate to conditions at the site? We start by examining the assumptions given above. First, the order of these reactions and whether reaction order is uniform across the shelf is, at present, unknown. First-order reaction kinetics was assumed for purposes of the modeling in the absence of evidence to the contrary (22), but there is no *a priori* reason to reject the possibility of higher or lower reaction orders, let alone spatial variation of reaction order. This assumption remains to be tested.

The second assumption, that no competing reactions are involved, is more difficult to assess directly. We compared the summed molar whole-core inventories of p,p' -DDE, p,p' -DDMU, and p,p' -DDNU in the two 124B1 cores and found that they came within ~21% of each other (Figure S9). The apparent “deficit” in the 2003 core is near the level of analytical uncertainty (~19%) and appears to be associated with differences in p,p' -DDE concentrations (Supporting Information, section 8). If real, the “deficit” might indicate that other reactions are occurring. The lack of any p,p' -DDT in the sediments by 1992 (22) means that a supply of diagenetically formed p,p' -DDE (via dehydrochlorination of p,p' -DDT) no longer existed. Sources of p,p' -DDMU and p,p' -DDNU other than p,p' -DDE and p,p' -DDMU, respectively, can be postulated (Figure S2). However, production of p,p' -DDMU from p,p' -DDD (and by inference, p,p' -DDNU from p,p' -DDMS) seems unlikely for two reasons. First, the change in molar inventory of p,p' -DDD from 1992 to 2003 ($-0.014 \mu\text{mol}/\text{cm}^2$) is insufficient to account for the increase in p,p' -DDMU during this period ($+0.077 \mu\text{mol}/\text{cm}^2$; (22)). Assuming p,p' -DDMU is transformed to p,p' -DDNU, the decrease in inventory of p,p' -DDD can explain even less of the gross increase in inventory of p,p' -DDMU. Second, microcosm experiments with PVS sediment showed that p,p' -DDD was not a significant source of p,p' -DDMU (19). The possibility that p,p' -DDE, p,p' -DDMU, or p,p' -DDNU might have become incorporated into a nonextractable fraction of the sediments is deemed unlikely (section 8, Supporting Information).

The third assumption, that transformation rates do not change with time, cannot be easily tested with available data. At or near station 3C, rates of reductive dechlorination appear to have changed over the past decade to decade and a half. This is indicated qualitatively by the greatly increased percent of p,p' -DDMU in the 2003 core compared to the 1992 core over a period of only 11 years (Figure 1). Using the mean first-order p,p' -DDE transformation rate of 0.052 yr^{-1} and hindcasting from 1992 to 1981, we obtain an inventory at the study site of $1.21 \mu\text{mol}/\text{cm}^2$. The measured inventories of p,p' -DDE in cores collected by the LACSD at station 3C in 1981 were $1.6\text{--}1.8 \mu\text{mol}/\text{cm}^2$ (5). This would seem to indicate that rates may actually have been somewhat higher between 1981 and 1992 than they were from 1992 to 2003. However, this simple comparison relies on data from cores that were collected and analyzed using significantly different methods. Nevertheless, it seems probable that dechlorination rates could change in the future, not only at or near station 3C but in other locations.

Finally, the model assumes that no other processes are responsible for losses of parent or daughter products. Losses of these compounds in surficial layers of the sediment column due to the combined effects of mixing, resuspension, and desorption will undoubtedly occur at all locations along the shelf (11, 13). However, the extent to which these processes result in significant losses within the sediment column at a given location is limited by the numbers, activities, and distribution of resident infauna (12, 16); the degree of pelletization of the sediment (44, 45); and the frequency, intensity, and duration of storm events (46). The bulk of the

existing inventory of DDT compounds in the most heavily contaminated sediments (e.g., along the 60-m isobath) is now buried at depths below those where the most intense mixing and resuspension are likely to occur (Figure 3; 7, 16). Thus, *in situ* degradation at the study site is expected to be one of the most important, if not the dominant, removal processes for the foreseeable future (13). One possible mitigating factor is the presence and activities of thalassinid shrimp, whose burrows can reach depths where sediment contamination is high (16). These shrimp have been observed more frequently in the vicinity of station 3C than at locations nearer the outfall. Transport of sediment from deep, heavily contaminated layers during burrow excavation would serve to mobilize sediments and make associated contaminants available for loss through the aforementioned processes. Judging from the nearly identical vertical concentration profiles of conservative waste-derived contaminants, such as the PCBs, deep bioturbation did not occur in the cores collected near station 3C in 1992 and 2003.

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Supporting Information Available

Site maps, transformation pathways, PCB target analytes, PCB dechlorination assessment, core alignment procedures, transformation rate calculations, multistep reaction modeling, and DDT mass balance calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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