cally 1.3 to 1.6 km (3), and on the southern EPR the axial magma body appears to lie within 1 km below the sea floor in some areas. Phipps Morgan and Chen (22) have described conditions where the accumulation of melt in these bodies is controlled thermally by the balance of magmatic heat input and hydrothermal cooling. They have shown that under these conditions a variation in the depth of the axial melt lens with spreading rate is expected if the fraction of heat removed by hydrothermal circulation remains constant with spreading rate. Taken together, the results from our study provide strong additional support for the emerging view that crustal magma chambers along intermediate- and fast-spreading ocean ridges consist of small, sill-like midcrustal bodies that overlie a broader, largely solidified lower crustal section.

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1. The seismic structure of oceanic crust is typically divided into two major layers. The upper crust, layer 2, is characterized by a rapid increase in *P*-wave velocities from <2.5 to >6 km s^{-1}. Layer 2, which has a thickness of ~2 km, is sometimes subdivided into layers 2A, 2B, and 2C. The lower crust, layer 3, is about 5 km thick and is associated with much lower velocity gradients (<1 s^{-1}) and *P*-wave velocities of 6.5 to 7.0 km s^{-1}. The lithologic interpretation of this seismic layering is still not certain. However, layer 2 is generally believed to be made up of extrusive lava flows that grade downward into a sheeted dike complex, whereas layer 3 is interpreted as plutonic rocks such as gabbro, cumulate gabbro, and cumulate ultramafics.
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In Situ Stimulation of Aerobic PCB Biodegradation in Hudson River Sediments

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A 73-day field study of in situ aerobic biodegradation of polychlorinated biphenyls (PCBs) in the Hudson River shows that indigenous aerobic microorganisms can degrade the lightly chlorinated PCBs present in these sediments. Addition of inorganic nutrients, biphenyl, and oxygen enhanced PCB biodegradation, as indicated both by a 37 to 55 percent loss of PCBs and by the production of chlorobenzoates, intermediates in the PCB biodegradation pathway. Repeated inoculation with a purified PCB-degrading bacterium failed to improve biodegradative activity. Biodegradation was also observed under mixed but unamended conditions, which suggests that this process may occur commonly in river sediments, with implications for PCB fate models and risk assessments.

Polychlorinated biphenyls undergo biodegradation under a variety of conditions in the laboratory and in aquatic sediments (*1*, *2*). Two classes of bacteria with PCB-transforming capabilities have been identified. Anaerobic bacteria that dechlorinate PCBs typically attack the higher chlorinated PCB congeners through reductive dechlorination (*3*), a process that removes chlorines but leaves the biphenyl rings intact. This process has occurred extensively in a number of sediments (*3–5*), which results in a reduction in higher chlorinated PCB congeners and a commensurate increase in lower chlorinated congeners. Similar selective shifts in PCB congener distributions have been reproduced in laboratory experiments with anaerobic sediment slurries that contained active microbial populations (*6*, *7*).

The less chlorinated PCB congeners produced by anaerobic dechlorination are suitable substrates for oxidative degradation by a wide range of aerobic organisms (*8–12*). The predominant mechanism in the enzymatic pathway for oxidative PCB biodegradation involves an initial 2,3-dioxygenase attack, followed by oxidation through a second dioxygenase and ring cleavage (*8*). Products of this pathway include the corresponding chlorobenzoic acids, which are readily degraded by other aerobic bacteria (*13*, *14*).

Although much is known about the oxidative degradation of PCBs by aerobic bacteria in laboratory experiments (*1*, *2*), little is known about this process in the field. To that end we performed an in situ PCB bioremediation experiment in a river sediment environment. The objectives of the study were to demonstrate that aerobic PCB biodegradation can occur under field conditions and to identify the key variables that influence the rate and extent of PCB biodegradation in Hudson River sediments.

Several criteria were used to assess the extent to which in situ biodegradation is responsible for PCB losses in Hudson River sediments (*15*): (i) the use of controls to distinguish between biotic and abiotic losses, (ii) quantitation of the loss of coreactants that participate in the biodegradation process (O_2 and biphenyl), (iii) enumeration of PCB-degrading microbial populations that correlate with in situ biodegradation, (iv) observation of the selective disappearance of microbially labile PCB congeners, and (v) detection of metabolic intermediates (chlorobenzoates).

The field study was conducted immediately offshore from the west bank of the Hudson River in the town of Moreau, New

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York, 312 km upstream from New York City. The surface sediment was a sandy silt with a highly variable PCB content (average of 39.4 mg kg^{-1}, SD of 102 mg kg^{-1}). Chromatographic analysis showed that most of the PCBs resided in the top 10 to 20 cm of the sediment and had undergone extensive in situ dechlorination (62 to 73% mono- and dichlorobiphenyls) relative to the commercial PCB mixture originally released into the river (predominantly Aroclor 1242 that contained 9% of these congeners).

We studied the effects of the mixing mode and the addition of O_2, inorganic nutrients (ammonia-nitrogen and phosphate), biphenyl, and PCB-degrading bacteria on in situ aerobic PCB biodegradation. The experiments were conducted in six self-contained steel caisson reactors (R101 to R106) that were driven into the river bottom to isolate the natural biota and sediment from the river environment (Fig. 1). With a sediment corer 5 cm in diameter (*16*), 12 cores were taken from each caisson at the beginning and end of the study and four cores per caisson were taken weekly. In addition, aqueous and sediment samples were taken throughout the study for bacterial counts (*17*) and chlorobenzoate and biphenyl analyses.

The experiment began on 9 August 1991 and ran for 73 days. Before that time the sediments in the caissons were premixed for 24 hours to homogenize the contents. Water temperature and pH in the caissons were monitored but not controlled. Caisson temperatures tracked ambient river temperatures, which ranged from 28°C on 30 August to 10°C on 21 October. The pH in all the caissons stayed between 6.0 and 7.0, with the exception of high-mix caisson R102, where the pH fell rapidly and remained below 5.0 for most of the experiment. Increased biological nitrifying activity was observed in R102 and accounts for the drop in pH (63 mg of nitrate per liter were produced in R102 versus 3 to 5 mg $liter^{-1}$ in other caissons).

Dissolved O_2 concentrations, in the water column for the experimental caissons were maintained at 6.0 to 6.5 mg $liter^{-1}$. Low-mix control caisson R104 remained anaerobic throughout the study, whereas the high-mix control R101 became aerobic through incorporation of O_2 from the headspace at the high rate of mixing. Purging this caisson with 2 to 4 liters of liquid N_2 partially mitigated this effect and reduced dissolved O_2 concentrations to <2 mg $liter^{-1}$. The total peroxide usage in the low-mix experimental caissons ranged from 182 to 197 liters of 10% peroxide solution. These volumes are close to the theoretical biological O_2 demand (BOD), on the basis of initial sediment BOD values (500 mg kg^{-1}) and on the assumption of complete biphenyl consumption. Peroxide usage in R102 was 50% greater than in the other caissons, which reflects the additional O_2 demand associated with the enhanced biological nitrifying activity.

In response to the addition of O_2 and nutrients, the numbers of indigenous biphenyl-metabolizing microorganisms that were measured in aqueous samples by plate counts increased by at least six orders of magnitude in all the experimental caissons, independent of inoculation with *Alcaligenes eutrophus* H850, a PCB-degrading bacterium. Populations in the three low-mix experimental caissons increased from $<10^2$ to a maximum of 10^8 colony-forming units (cfu) per milliliter 3 weeks into the study, whereas the population in R102 increased more slowly, reaching 10^8 cfu ml^{-1} by day 60. Population increases were not observed in samples from the control caissons.

The survival of *A. eutrophus* H850 was generally poor during the experiment. Caissons R102 and R103 were inoculated two or three times each with H850 to yield a target concentration of 10^8 cells per milliliter. Typical concentrations after inoculation ranged from 10^7 to 10^8 cfu ml^{-1}. After each addition, the concentration of H850 dropped below 10^5 cfu ml^{-1} within 10 days of inoculation.

The indigenous biphenyl-metabolizing microbial populations in the caissons were active against the lightly chlorinated PCB congeners present in upper Hudson sediments. Several isolates were selected to compare their PCB-degradative competence with that of H850 in resting cell assays (*12*) (Fig. 2). Most isolates could not degrade the more highly chlorinated PCB congeners as efficiently as H850 but were capable of readily degrading the mono- and dichlorobiphenyls (for example, 2 CB, 4 CB, 2-2 CB, 23 CB, 2-3 CB, and 2-4 CB) prevalent at the test site.

Substantial caisson-to-caisson variability in initial PCB concentrations was due to the heterogeneous manner in which PCBs were distributed over the test site (Table 1). Large SDs in the PCB values at start time t_0 indicate that significant heterogeneity also existed within the caissons even after premixing. Statistically significant changes (95% confidence level) in average PCB concentrations were observed in all caissons except high-mix control R101. However, the apparent PCB loss of 41.8% observed in R104, the low-mix control, complicates the interpretation of these results. Steps to assess the impact of abiotic processes included: (i) analysis of vapor traps to monitor volatilization, (ii) analysis of samples below the well-mixed sediment zone to monitor dilution, (iii) use of swipe samples to evaluate adherence of PCBs to the vessel walls, and (iv) investigation of potential PCB losses through Fenton chemistry (*18*). No significant PCB losses occurred by any of these abiotic routes.

We attribute the apparent PCB loss in R104 to sampling difficulties in the low-mix caissons. Attrition of the sediment particles caused by the slow movement of the rakes caused an increase in PCB-rich suspended

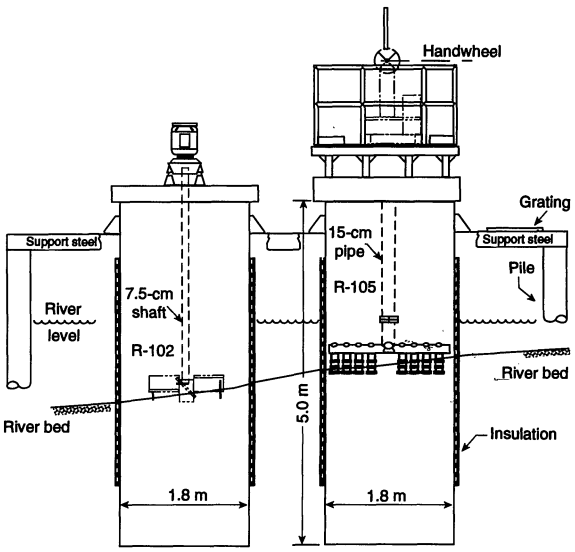

Fig. 1. Side view of the research platform. The research platform was an 8 m by 12 m rectangular steel structure erected ~3 m offshore that supported six steel caisson reactors. Two of the caissons (R101 and R104) were controls for two types of agitation systems [high-mix, turbine (40 rpm) and low-mix, rake (3 rpm), respectively]. In each case, only the top 15 to 20 cm of sediment was mixed. No nutrients, O_2, or microorganisms were added to these caissons to limit aerobic biological activity. Aerobic conditions were established in four caissons by automatically controlled addition of hydrogen peroxide. Ammonia-nitrogen, phosphate, and biphenyl were added at the start and at intervals throughout the study (*34*). The use of biphenyl as a growth substrate induces maximal PCB-degradative activity in bacterial strains in the laboratory (*35*). Among caissons, R102 contained a high-mix agitator, whereas other caissons (R103, R104, and R106) had low-mix systems. Two caissons (R102 and R103) were inoculated (*36*) with *Alcaligenes eutrophus* H850 bacteria. It was originally isolated from PCB-containing dredge spoils upstream from the test site and degrades an unusually broad spectrum of PCB congeners (*21, 37*). R105 and R106 were duplicate caissons in which only the indigenous bacterial populations were stimulated. All the caissons were vented to the atmosphere through vapor traps that contained XAD-2 resin to retain any volatilized PCBs.

organic matter that did not settle readily before sampling. Two low-mix caissons (R104 and R105) were sampled again (n = 6) after an additional week of settling at the end of the experiment. Improved PCB mass balance was achieved in R104 (average PCB concentration = 48.9 ± 4.8 mg kg^{-1}), whereas a PCB loss of 50% was observed in caisson R105 (average PCB concentration = 24.8 ± 4.8 mg kg^{-1}).

A better assessment of the extent of biodegradation in the field involves monitoring the ratio of readily degraded compounds to more recalcitrant compounds in the contaminant mixture (*19, 20*). Changes in this ratio can be used to estimate losses that are directly attributable to biological activity. Several congeners in PCB mixtures do not biodegrade easily under aerobic conditions, although almost all congeners in the Aroclor 1242 commercial mix are susceptible to some aerobic biodegradative attack (*21*). Losses that are based on ratio changes in selected PCB reference peaks would be a conservative estimate of the total PCB biodegradation in the system. PCB losses were recalculated with peak 61 (34-34 CB/236-34 CB) as a reference peak (Table 1). Statistically significant changes were observed in all caissons except R104. Other peaks selected for this procedure (39, 48, and 82) gave similar results. Losses in all of the experimental caissons converge to ~40% by this analysis. A statistically significant congener-specific PCB loss of 14.4% was also observed in high-mix control caisson R101. This result suggests that some aerobic PCB-degradative activity may have occurred in R101, stimulated by the low concentrations of O_2 in the aqueous phase of this caisson throughout the experiment.

Comparison of PCB congener peak profiles at t_0 and end time t_f indicates that congener-specific changes typical of aerobic biodegradation took place in all of the experimental caissons and in control caisson R101 (Fig. 3, A to D). For example, significant reductions were evident in 2 CB, 2-2 CB/26 CB, 23 CB/2-4 CB, and 236 CB/26-3 CB (peaks 2, 5, 8, and 16) in these caissons. A PCB degradation pattern with a broader range was observed in R102, as indicated by additional PCB losses in peaks 10 (26-2 CB), 14, 15, 17, 19, 21 to 26, and 31 that contained predominantly trichlorobiphenyl congeners. Although this wider degradative competence may have been due to the presence of H850 in R102, the unique environment created in that caisson may have stimulated an indigenous PCB-degrading population with broader congener specificities. The small congener-specific losses observed in R104 are not consistent with known biodegradative specificity or any other congener-specific loss mechanism.

PCB concentrations were also normalized to the total organic carbon (TOC) measured in the sediment. Detailed analysis of sectioned cores indicates that a large percentage of the PCBs resided in the lighter, highly organic phase of the sediment. This result was expected because hydrophobic contaminants tend to partition into organic matter in natural systems (*22, 23*). All t_0 and t_f sediment samples were homogenized, subsampled, and analyzed for solid-phase TOC content (*24*). On the basis of TOC content, PCB concentrations were recalculated from these results (Table 1). Statistically significant reductions in TOC-based PCB averages at t_f occurred in all the experimental caissons, with losses ranging from 45 to 55%. Changes in these values in control caissons R101 and R104 were not statistically significant at a 95% confidence level.

Weekly samples were used to estimate the rates of PCB biodegradation in the caissons. Peak 61 normalized averages were used because this analysis was least affected by sample heterogeneity. In general, the initial PCB biodegradation rates observed in our field study (0.09 to 0.48 mg kg^{-1} day^{-1}) were two to three times slower than those in model systems in the laboratory, although the overall extent of biodegradation observed was comparable (*25*). These differences in loss rates may be due partly to

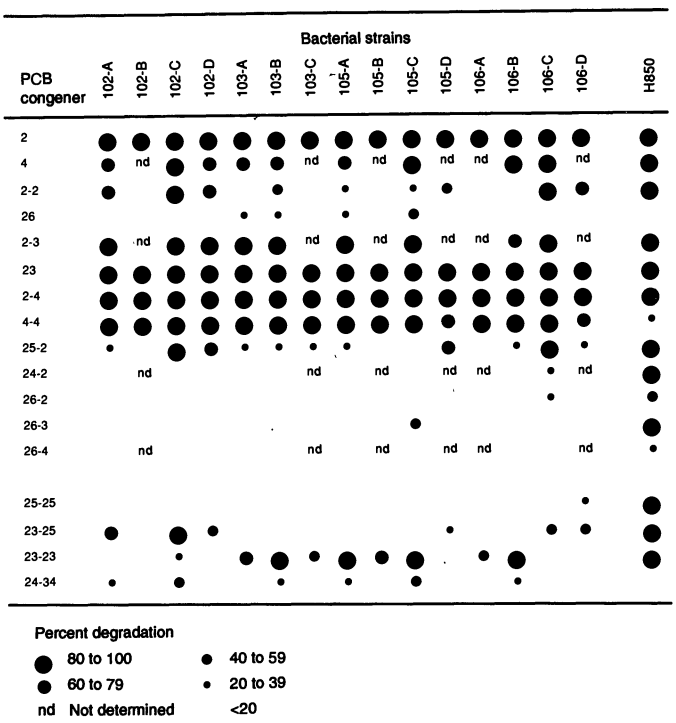

Fig. 2. PCB-biodegradative competence of bacteria isolated from sediments in Hudson River research station caissons. Individual PCB congeners are designated by numbers that indicate the substitution pattern on each ring, separated by a dash. Thus, 2,2',6-chlorobiphenyl (CB) is referred to in this paper as 26-2 CB. Several biphenyl-degrading populations were present in the caissons, on the basis of morphological differences in colony appearance observed during plate-count assays. Several of these colonies were selected to compare their PCB-degradative competence with that of H850. Resting-cell assays (*12*) of these biphenyl-metabolizing isolates were performed with defined PCB-congener mixes (0.5 μM per congener) that included the lower chlorinated PCB congeners that predominate at the study site. PCB analysis was performed by gas chromatography electron-capture detection with a DB-1 or SB-Octyl-50 (Lee Scientific, Salt Lake City) capillary column (50 m long with an 0.2-mm inner diameter) (*38*) when necessary to quantitate congeners (for example, 2-2 CB and 26 CB) that co-elute on the DB-1 column.

Table 1. Summary of PCB analyses of core samples taken at the start (t_0) and end (t_f) of the study. Three different methods of quantifying PCB concentration [PCB] are shown. Average PCB concentrations are given on a sediment dry-weight basis (column 1), normalized to congener peak 61 (column 2), and normalized to total organic carbon (TOC) in the sediment (column 3). Results are given as averages ±1 SD (n = 12). Percent changes between t_0 and t_f concentrations are also shown.

Caisson	[PCB] (mg kg^{-1})	PCB/peak 61 (mg kg^{-1})	PCB/TOC (mg g^{-1})
R101, t_0	6.0 ± 1.9	6.0 ± 1.0	0.6 ± 0.2
R101, t_f	6.5 ± 2.5	5.1 ± 0.4	0.4 ± 0.3
Change	+8.7%*	−14.4%	−30.7%*
R102, t_0	20 ± 11	20 ± 2.0	1.4 ± 0.4
R102, t_f	12 ± 7.3	12 ± 2.6	0.8 ± 0.4
Change	−41.0%	−42.4%	−44.7%
R103, t_0	30 ± 11	30 ± 2.8	1.8 ± 0.7
R103, t_f	19 ± 5.0	19 ± 1.4	0.8 ± 0.2
Change	−36.8%	−37.8%	−55.5%
R104, t_0	40 ± 16	40 ± 4.8	1.7 ± 0.4
R104, t_f	23 ± 9.9	38 ± 3.3	1.8 ± 1.1
Change	−41.8%	−4.3%*	+8.4%*
R105, t_0	50 ± 28	49 ± 4.7	2.1 ± 0.6
R105, t_f	14 ± 5.6	29 ± 3.3	1.0 ± 0.2
Change	−72.6%	−40.5%	−53.1%
R106, t_0	39 ± 18	39 ± 2.7	1.8 ± 0.7
R106, t_f	12 ± 4.1	24 ± 2.0	1.0 ± 0.2
Change	−68.5%	−38.7%	−46.0%

*Changes that were not statistically significant at the 95% confidence level with a two-sample t test.

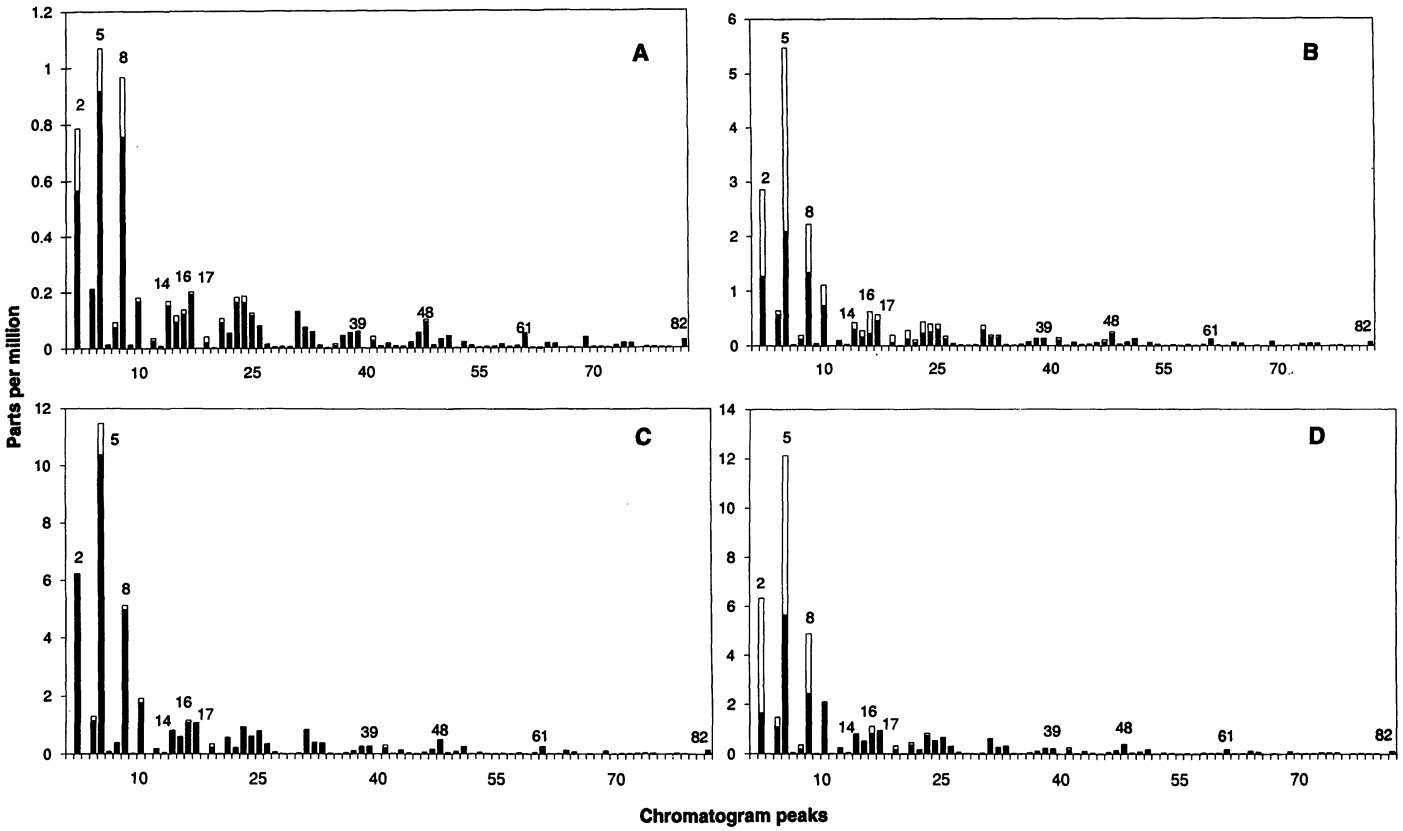

Fig. 3. Histogram showing peak-specific PCB concentrations in core samples from caisson (**A**) R101, (**B**) R102, (**C**) R104, and (**D**) R106 at t_0 and t_f. Histograms represent averages of all 12 cores taken at that time, normalized to peak 61. Solid bars, day 73; hollow bars, day 0. Normalization was done by calculation of the average PCB concentration of the selected reference peak at t_0, under the assumption that this concentration did not change over the course of the experiment. R106 is representative of all the low-mix experimental caissons. Selected PCB congener peak identifications are: 2 (peak 2); 4 (peak 4); 2-2/26 (peak 5); 24/25 (peak 6); 2-3 (peak 7); 23/2-4 (peak 8); 26-2 (peak 10); 25-2/4-4 (peak 14); 24-2 (peak 15); 236, 26-3 (peak 16); 23-2/26-4 (peak 17); 236-4/26-34 (peak 39); 2356-2/236-25 (peak 48); 34-34/236-34 (peak 61); and 234-245/2356-34 (peak 82).

differences in length scale and mixing between the field and the laboratory.

With a sensitive gas chromatography–mass spectrometry (GC-MS) method, chlorinated benzoates were detected as transient intermediates in the aqueous phase of all of the experimental low-mix caissons (Fig. 4) (*26*). In general, the monochlorobenzoates appeared earlier (10 to 20 days) than the dichlorobenzoates (15 to 35 days). The formation of these metabolites coincided with increased populations of indigenous biphenyl-metabolizing bacteria and correlated with the selective disappearance of specific PCB congeners (Fig. 3). The expected degradation product of 2 CB, 2-2 CB, 2-3 CB, and 2-4 CB is 2-chlorobenzoate (CBA). These four congeners represented 55 to 60% of PCBs in the sediment, which explains the large proportion of 2 CBA observed in the caissons. Degradation of 4 CB and 2-4 CB can produce 4 CBA. The low concentrations of 24 CBA and 25 CBA that we detected are expected degradation products of 24-2 CB, 24-3 CB, and 24-4 CB and of 25-2 CB, 25-3 CB, and 25-4 CB, respectively. Accumulation of 26 CBA was not observed, presumably because only small amounts of the dichlorinated PCB congener (26 CB) and one (26-3 CB) of the trichlorinated PCB congeners (26-2 CB, 26-3 CB, and 26-4 CB) that are capable of producing this intermediate were degraded in the low-mix caissons during the experiment. Increased chlorobenzoate levels were not detected in the corresponding low-mix control, R104.

The transient nature of the detected chlorobenzoates was expected because these intermediate compounds are further metabolized by many naturally occurring microorganisms (*13, 14*). Such aerobic chlorobenzoate-degrading microorganisms were isolated from Hudson River sediments and showed good degradative competence in the laboratory against a range of chlorobenzoates including 2 CBA, 3 CBA, 4 CBA, 24 CBA, 25 CBA, 26 CBA, and 35 CBA (*26*).

Elevated chlorobenzoate concentrations did not occur in the aqueous phase of either high-mix caisson, although significant PCB losses were observed. It is possible that the

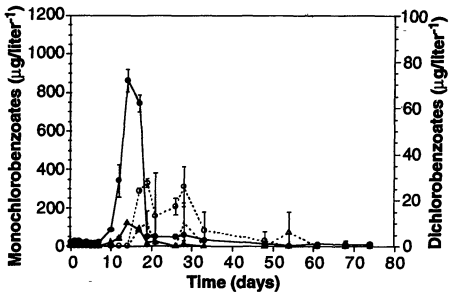

Fig. 4. Aqueous-phase chlorobenzoates: congener-specific mono- and dichlorobenzoates in R106. R106 is representative of all the low-mix experimental caissons. Points represent average values for two analyses with ranges shown. Filled circles: 2 CBA; filled triangles: 4 CBA; hollow circles: 2,5 CBA; hollow triangles: 2,4 CBA. Aqueous samples were acidified, extracted into anhydrous ethyl ether, derivatized with pentafluorobenzyl bromide (*39*), and analyzed for chlorobenzoates by GC-MS with a Hewlett-Packard 5890 gas chromatograph equipped with a DB-1 column and a quadrupole mass-selective detector. Selected ion monitoring was used to quantify the concentrations of the mono- and dichlorobenzoate congeners in each sample extract (*26*). In this analysis, 3 CBA and 4 CBA were not resolved, although 3 CBA should not be a significant PCB-degradation product on the basis of the initial PCB-congener distributions in the caissons.

rapid mixing may have created favorable conditions for early stimulation of the indigenous chlorobenzoate-degrading microbial population so that these intermediates were not detectable.

No more than 60% of the PCBs in Hudson River sediments were biodegraded in both field and laboratory experiments. However, nearly all (>90%) of this material should be biodegradable, on the basis of past laboratory experiments with these same congeners in the absence of sediment (*21, 27*). A short-term biodegradation limit in both the laboratory and the field may be physically determined by the desorption kinetics of the PCBs from the sediments. Many nonionic organic compounds display bimodal desorption kinetics when they are sorbed to soils or sediments. A labile component of the organic compound desorbs readily, whereas the desorption of a resistant component is orders of magnitude slower (*28, 29*). This phenomenon has been observed with both PCB-spiked and environmentally contaminated sediments (*30, 31*), with ~50% of the PCBs in Hudson River sediment residing in the resistant component (*32*).

The resistant fraction probably consists of PCBs that are dissolved in the polymeric, natural organic matrix of the sediment and must diffuse through this matrix before desorption can occur (*29*). It is likely that this resistant PCB fraction is not available to microorganisms in its sorbed state and therefore represents the primary limitation to the biodegradation process. This diffusion process may also limit uptake by other organisms (*33*) and has important implications for the determination of risk estimates. Although the resistant PCB fraction is expected to become available over long periods of time (months or years), physical, chemical, and natural aerobic biodegradative processes should lessen the effects of this slowly desorbing material.

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16. Before samples were taken, the mixers were turned off to allow the sediment to settle. Settling times were 24 to 48 hours at t_0 and t_f and 3 to 6 hours during weekly sampling. The top 10 to 15 cm of sediment in the cores was homogenized and analyzed. PCB analysis was done by Northeast Analytical Laboratory (Schenectady, NY). PCBs were Soxhlet-extracted from the sediment, and the extracts were treated with elemental mercury to remove sulfur, sulfuric acid to remove polar compounds, and florisil as a final clean-up step. PCB analyses were performed on two Varian 3400 gas chromatographs with DB-1 (J & W Scientific), bonded polydimethylsilicone, fused silica capillary columns (30 m long with a 0.25-mm inner diameter), and electron capture detectors. With this column system 118 PCB peaks can be resolved [J. F. Brown, Jr., *et al.*, *Environ. Toxicol. Chem.* **6**, 579 (1987)].
17. Within 24 hours of removal, samples were diluted and plated on agar medium by standard plating techniques [*Standard Methods for the Examination of Water and Wastewater*, L. S. Clesceri, A. E. Greenberg, R. R. Trussell, Eds. (American Public Health Association, Washington, DC, ed. 17, 1989)]. Phosphate ammonium salts (PAS) minimal media plates with biphenyl crystals in the cover of the petri dish were used to estimate the concentration of bacteria that could using biphenyl as the sole source of C for growth (biphenyl-metabolizing bacteria) [F. J. Mondello, *J. Bacteriol.* **171**, 1725 (1989)]. PAS-biphenyl plates were inverted and incubated at 28°C for 4 to 10 days, depending on the growth rate of the colonies observed. H850 could be distinguished from the indigenous biphenyl-metabolizing population in plate-count assays by its distinct morphology and rapid growth on biphenyl. Biochemical assays were used to verify these assignments (Biolog, Haywood, CA).
18. A recent paper [D. L. Sediak and A. W. Andren, *Environ. Sci. Technol.* **25**, 1419 (1991)] described the nonselective hydroxylation of PCB congeners and mixtures by Fenton's reagent ($H_2O_2 + Fe^{2+} \rightarrow OH^{\cdot} + Fe^{3+} + OH^-$). This reaction was judged not to contribute significantly to the PCB losses observed in this study for the following reasons: (i) Near neutral pH, the decomposition of H_2O_2 to H_2O and O_2 is catalyzed by Fe^{3+} with an apparent rate constant five times greater than that for radical formation [M. J. Clifton and A. Savall, *J. Appl. Electrochem.* **16**, 812 (1986)]. At the electrochemical potential of the water in the caissons, Fe^{2+} is not thermodynamically stable and the equilibrium concentration of Fe^{3+}, as $Fe(OH)_2^+$, would be six to seven orders of magnitude greater than that of Fe^{2+} [M. Pourbaix, in *Atlas of Electrochemical Equilibria in Aqueous Solutions* (National Association of Corrosion Engineers, Houston, TX, 1974), pp. 309–313]. (ii) The decomposition of H_2O_2 to H_2O and O_2 that is catalyzed by bacterial catalase is six orders of magnitude faster than that for radical formation [H. Hatzikonstantinou and S. B. Brown, *Biochem. J.* **174**, 893 (1978)]. (iii) Hydroxy radicals react rapidly with dissolved natural organic matter. (iv) The biphenyl added to the caissons was 50 times more abundant than the PCBs. GC-MS analyses of the water from several caissons found only small amounts (<0.5 mg liter^{-1}) of monohydroxybiphenyl, which were hydroxylated only in the ortho and para positions. The absence of meta hydroxylation implicates an alternate oxygenase pathway rather than the nonselective hydroxylation due to Fenton's reagent.
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24. TOC analyses were done by Hudson Environmental Services (Queensbury, NY) with the use of procedures outlined in Environmental Protection Agency (EPA) Method SW846-9060 and the EPA Lloyd Kahn method.
25. Shake-flask and 1-liter reactor studies of PCB biodegradation in Hudson River sediments were performed before the field study under conditions that approximated those in the field [*1991 In Situ Hudson River Research Study*, D. A. Abramowicz, M. R. Harkness, J. B. McDermott, J. J. Salvo, Eds. (GE Corporate Research and Development, Schenectady, NY, 1992)]. Experiments with PCB-contaminated sediments nominally lasted 4 weeks and were performed at room temperature. Nutrient and biphenyl ammendments and H850 inoculations bracketed the levels used in the field study. Biodegradation losses were compared to PCB recoveries obtained from killed controls. PCB biodegradation losses ranged from 30 to 63% in these studies.
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32. The desorption kinetics of PCBs from environmentally contaminated Hudson River sediment were examined with XAD-4 (Rohm and Haas polystyrene bead resin) as a PCB sink. Sediment samples were contacted with resin and mixed on a reciprocating shaker while PCB transport between the sediment and resin phases was monitored. In the first 170 hours of mixing, 50% of the PCBs desorbed from the sediment. Over a period of 6 months, an additional 50% of the PCBs that made up the resistant fraction slowly desorbed from the sediment with uptake by the resin [*1991 In Situ Hudson River Research Study*, in (*25*)].
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