Settling Removal Rates of PCBs into the Northwestern Atlantic Derived from ^{238}U—^{234}Th Disequilibria

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Surface ocean export fluxes of polychlorinated biphenyls (PCBs) were deduced utilizing ^{234}Th as an indicator of the removal rates of particle-bound species from coastal, continental shelf, and pelagic surface waters. The fraction of the PCB settling flux that reaches the sediments (the ratio of bottom sediment import flux to ^{234}Th-derived surface ocean export flux) decreased with both water column depth and with aqueous solubility of the congeners, presumably as a result of particle decomposition and/or compound desorption. A sharper decrease in ^{234}Th-derived surface ocean fluxes away from the continental source was seen for congeners with increasing chlorination. This suggests that atmospheric washout followed by particle-mediated settling out of the surface ocean are the predominant processes affecting the PCBs, as opposed to atmospheric hydroxyl radical-mediated decomposition. Based on this limited data set, the largest fraction of each PCB is removed into the open ocean, although higher areal fluxes are seen closer to the coast. For example, we estimate that 14 000 mol yr^{-1} of a tetrachlorobiphenyl (congener 52) were sequestered in the northwestern Atlantic Ocean in 1993−1994, with 75% of the flux being in the pelagic sector, 20% on the continental shelf, and only 5% in the 20-km-wide coastal region closest to the continental source.

Introduction

Continued research on the environmental behavior and fate of polychlorinated biphenyls (PCBs) is warranted due to the environmental longevity and high toxicity of many PCB congeners (*1*, *2*). While PCB production ended 20 years ago, ecotoxicologically significant PCB concentrations remain in the contempory environment (*2*). There is currently a debate over whether PCB levels in the biosphere continue to decrease (*3*−*5*) or whether they have attained steady-state concentrations (*6*, *7*). To increase our understanding of the global fate of PCBs, we need congener-specific estimates of their fluxes into long-term and permanent sinks. These sinks include settling removal on particles into the ocean interior, sediment and soil burial, as well as microbial degradation and abiotic environmental transformations, such as vapor-phase reactions with hydroxyl radical.

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Flux data for individual PCB congeners have been predominantly derived from estimates of atmospheric deposition, surface water volatilization, or sedimentation through relatively shallow and annually destratified lakes (e.g., refs 8−15). Several mass balance studies based on such data have provided valuable insights into the rates of PCB cycling between different compartments in the contempory environment (e.g., refs 4, 16, 17), but these are less informative regarding the larger-scale and longer-term fate of PCBs. North America and Europe are believed to be the dominant global source areas for PCBs based on historical records of their manufacture and usage (*18*−*22*), and the North Atlantic Ocean has been discussed as their dominant final repository (*20*, *21*, *23*, *24*). However, quantification of the PCB flux into the ocean interior and to the sediments of the North Atlantic Ocean has proved elusive for two major reasons. First, it is a significant analytical challenge to measure accurately trace-level concentrations of individual PCB congeners in seawater (*24*−*27*). Secondly, reliable methods to estimate the downward flux of organic pollutants from the surface ocean are lacking (*28*, *29*). Here we report on a limited set of PCB ocean flux estimates made using a novel technique based on the coupling of PCB congener inventories in surface ocean particles with the corresponding mixed layer ^{238}U—^{234}Th radioactive disequilibria.

Systematics of Th-Derived PCB Flux Estimates. Geochemists have developed an arsenal of techniques that take advantage of natural and anthropogenic tracers to deduce large-scale chemical transport rates. Several of these methods involve the use of natural radionuclides to quantify chemical fluxes between environmental compartments. For example, air−water exchange phenomena have been evaluated using ^{226}Ra—^{222}Rn disequilibria (*30*). Similarly, the magnitude of the radioactive disequilibrium in the surface ocean between extensively particle-bound ^{234}Th (solid−water distribution coefficient, $K_d \approx 10^6$−10^7 L/kg; e.g., ref 31) and its much more water-soluble radiogenic source, ^{238}U ($K_d \approx 10^2$ L/kg; e.g., ref 32), contains information regarding the surface ocean export rate of particulate matter (e.g., refs 33 and 34). The radioactivity of ^{234}Th in the surface ocean reflects a balance between its formation via radioactive decay of ^{238}U and losses due to decay and removal on settling particles:

$$\frac{\partial[^{234}\text{Th}_{\text{tot}}]}{\partial t} = \lambda[^{238}\text{U}_{\text{tot}}] - \lambda[^{234}\text{Th}_{\text{tot}}] - k_{\text{settle}}[^{234}\text{Th}_{\text{part}}] \quad (1)$$

where ^{238}U$_{\text{tot}}$ and ^{234}Th$_{\text{tot}}$ are the total radioactivities (dpm m^{-3}) of ^{238}U and ^{234}Th, respectively; ^{234}Th$_{\text{part}}$ is the radioactivity (dpm m^{-3}) of ^{234}Th in the particulate fraction; and λ is the radioactive decay constant of ^{234}Th (0.0288 d^{-1}). k_{settle} is the overall rate coefficient (d^{-1}) for vertical transport on settling particles, and this net rate coefficient reflects a combination of processes such as aggregation, disaggregation, and particle sinking.

We have previously shown that the assumptions of steady state (i.e., $\partial[^{234}\text{Th}_{\text{tot}}]/\partial t) = 0$) and negligible horizontal advective and eddy diffusive transport are reasonable in pelagic, continental shelf, and most coastal regimes (*31*, *35*−*37*). However, during transient events such as phytoplankton blooms, a non-steady-state model can improve predictions (*35*). Also, horizontal transport may enhance the actual vertical particle flux at the near-coastal station of this study, necessitating the application of a two-dimensional flux model under certain conditions (*37*). Without such special cases, the rate constant for downward export of ^{234}Th-carrying settling particles may be derived from eq 1:

$$k_{settle} = \frac{\lambda(^{238}U_{tot} - {}^{234}Th_{tot})}{^{234}Th_{part}} \qquad (2)$$

Having used this approach to determine particle removal rates (i.e., k_{settle}) from surface waters, one may then derive areally averaged fluxes for other particle-reactive compounds in the same system. Thus, for PCBs we have

$$F_{PCB} = k_{settle}z_{mix}[PCB_{part}] \qquad (3)$$

where F_{PCB} is the net vertical removal flux of a PCB (pmol m^{-2} d^{-1}), z_{mix} (m) is the depth of the surface mixed layer, and [PCB$_{part}$] is the particulate PCB concentration (pmol m^{-3}).

The application of the $^{238}U-^{234}Th$ systematics to derive fluxes of other particle-associated constituents, such as bulk organic carbon and nitrogen (36, 38) and polycyclic aromatic hydrocarbons (PAHs) (29), requires certain considerations. Since no filtration technique is believed to be able to separate quantitatively nonsettling (colloidal) from settling (gravitoidal) particles (39), it is important that the particulate PCB and ^{234}Th are obtained with similar filter cut offs and that this filterable ratio is representative of the ratio on true gravitoids (defined as particulate matter causing chemicals to be transported to a significant extent by gravitational settling; ref 39). Since the particle−solution distributions of both ^{234}Th (29, 31) and PCBs (e.g., ref 40) appear to be governed by the abundance of particulate organic carbon (POC) and since the settling carrier phases are largely aggregates of smaller particles−formed either by biological processes, such as fecal pellet packaging, and/or by physicochemical coagulation processes (e.g., refs 41−44)−the assumption of near-constancy of this ratio on different particle sizes appears reasonable.

A particularly beneficial aspect of the ^{234}Th-coupled technique for deriving upper ocean PCB export is that it is based on direct measurements of mixed layer properties. Estimates of surface ocean export from fluxes into sediment traps may be compromised by limitations in current trap technology and by the traps being positioned well below the surface mixed layer. The accuracy of flux estimates from shallow traps has been questioned based on a number of issues, including hydrodynamic biases, problems with preservation, and "swimmer" related artifacts (45, 46). Trap calibrations have reported both significant under- and overtrapping (up to factors of 3−10; refs 36 and 47). Furthermore, traps positioned at some greater depth would not be expected to quantitatively reflect surface ocean export fluxes due to desorption and organic matter remineralization processes during particle settling (e.g., refs 10 48, and 49). Attempts to relate bottom sediment fluxes of PCBs to export from surface waters are also complicated by the same water column processes. Fluxes estimated from sediments integrate over much longer time scales and are also sensitive to local sediment focusing and other diagenetic effects as well as to artifacts related to incomplete coretop recovery (ref 50, and specifically for PCBs, refs 10 and 51).

It is the objective of this paper to couple the surface water $^{238}U-^{234}Th$ disequilibria with measured particulate PCB concentrations to derive fluxes of these important xenobiotic compounds into the subsurface ocean. The stations sampled in this study include a range of regimes with varying intensities of particle sedimentation. While a greater spatial coverage would certainly be useful, extrapolations using these limited data allow an initial contrast of present annual removal rates of individual congeners into the North Atlantic Ocean with other large-scale estimates of long-term PCB sinks.

Experimental Methods

PCB Sampling and Analysis. We have previously described our sampling system (52) and shipboard methodology aimed

TABLE 1. Radionuclide Activities, Settling Rate Constants, and Mixed Layer Depths[a]

sample	distance (km)	^{234}Th (dpm/m^3) total	^{234}Th (dpm/m^3) particulate	^{238}U (dpm/m^3) total	k_{settle} (d^{-1})	z_{mix} (m)
93-4	2	117 ± 21	64 ± 4	2200 ± 22	0.94	8
93-2	15	217 ± 36	154 ± 7	2240 ± 23	0.38	15
94-4	2	504 ± 32	334 ± 19	1920 ± 19	0.12	8
94-2	15	778 ± 40	389 ± 21	2040 ± 21	0.093	15
94-1	110	1690 ± 53	308 ± 32	2330 ± 23	0.060	40
94-7	125	1810 ± 46	271 ± 26	2200 ± 22	0.042	35
93-BATS	1600	2270 ± 130	220 ± 10	2610 ± 26	0.044	28

[a] The location of the sampling stations were 93-4 and 94-4 at 43°40′ N 70°14′ W, 93-2 and 94−2 at 43°37′ N 70°07′ W, 94-1 at 42°38′ N 69°36′ W, 94−7 at 43°09′ N 69°51′ W, and 93-BATS at 31°50′ N 64°10′ W. Distance is given from nearest urban center (i.e., Portland, ME for stations 2 and 4; Boston for stations 1 and 7; and New York for station BATS). Settling rate constants were calculated from eq 2.

at minimizing both contamination and artificial sample fractionation (29). Briefly, water is pumped from the center of the mixed layer (Table 1) using an immersible low-internal-volume stainless steel pump with a small Teflon impeller (Fultz Pumps Inc., Lewistown, PA) through solvent-cleaned and seawater-preconditioned 1/4 in. (ca. 0.0063m) inner diameter high-grade stainless steel tubing. The sample (from 165 L at innermost coastal station to 657 L at outermost station near Bermuda) is filtered in-line through a precombusted GF/F glass fiber filter in a stainless steel holder (filters were replaced before cross-filter pressure drops exceeded 20 psi to minimize cell breakage). In a shipboard laminar-flow clean hood and using solvent-rinsed forceps, the filters were folded in half inward, transferred to precombusted Al foil envelopes, and stored frozen. The Gulf of Maine samples were collected in early September 1993 (93-4 and 93-2) and in late May 1994 (94-4, 94-2, 94-1, 94-7), while the Sargasso Sea sample (93-BATS) was obtained in early June 1993.

Sediment cores were obtained from a 0.25 m^2 by 0.7 m deep Sandia-Hessler MK-III box corer (Ocean Instruments, San Diego, CA). Samples were obtained from subcores that were extruded and processed for PCB (2−3 cm surface layer) and ^{210}Pb (entire sectioned core) analyses as decribed earlier (53).

For PCB analysis, the filters or sediments were spiked with four PCB internal standards (congeners 29, 97, 143, and 198), selected to be minor and easily identified components of industrial PCB mixtures. The samples were Soxhlet extracted for 48 h with a 9:1 mixture of dichloromethane−methanol (Ultra-Resi Analyzed Grade, J. T. Baker Inc.). After purification on a fully-activated silica column (54), the PCB fraction from the filters was analyzed using gas chromatographic high-resolution mass spectrometry (GCHRMS) at the Woods Hole Oceanographic Institution. On-column auto-injections (HP 7673 autosampler) of concentrated extracts respiked with an instrument injection standard (PCB 197) were performed onto a 30 m by 0.32 mm inside diameter (film thickness 0.25 μm) DB-5 capillary column (5% phenyl, J&W Scientific) housed in a HP 5890 Series II GC. The oven was temperature-programmed to start at 70 °C, ramp first at 20 °C/min to 180 °C, then ramp at 4 °C/min to 260 °C, and then finally to ramp at 20 °C/min to 310 °C followed by a 5-min hold. A VG Autospec EQ hybrid mass spectrometer was operated in positive electron ionization mode (ionization potential 50 eV, accelerating voltage 8000 V) and with a resolution of 1/10 000 D. Signals were acquired in grouped selective ion recording. The 15 target congeners, spanning a wide range of physicochemical properties, were selected because they either elute as single compounds (on a 5% phenyl column; ref 55) or in case of co-elution, they may be separately identified by HRMS because the major analyte has a different chlorination number than the interfering minor congener.

TABLE 2. Particulate Concentrations (fM) of Individual PCB Congeners in the Surface Ocean off Northeastern United States

congener[a]	concentrations (fM) at several ocean stations						
	93-4	93-2	94-4	94-2	94-1	94-7	93-BATS
26 (3)	n/a[b]	n/a	2.8	3.0	5.7	4.4	0.89
22 (3)	n/a	n/a	1.5	3.7	4.9	1.7	0.40
52 (4)	8.8	11	7.5	16	20	6.4	1.8
44 (4)	6.2	6.7	4.8	9.6	12	4.2	1.1
66 (4)	94	27	14	30	47	12	4.3
95 (5)	37	4.7	9.5	20	29	8.0	1.7
99 (5)	58	7.4	6.0	9.1	15	4.2	0.92
110 (5)	81	8.0	16	24	39	13	3.5
146 (6)	77	8.7	2.4	1.7	2.0	1.2	0.19
128 (6)	24	1.9	2.6	1.1	1.5	0.97	0.17
187 (7)	29	2.9	3.3	2.6	2.2	1.4	0.22
174 (7)	12	1.4	1.6	1.3	1.4	0.78	0.10
177 (7)	10	0.67	1.1	0.67	0.56	0.25	0.042
199 (8)	6.4	0.78	2.1	1.5	0.61	0.39	0.049
194 (8)	3.8	0.58	1.5	0.58	0.46	0.23	0.027

[a] See ref 55 to link congener number to structure. Numbers in parentheses refer to degree of chlorine substitution. [b] These trichlorinated congeners were *not* analyzed in these samples.

PCBs in sediment extracts were quantified using similar GC techniques but with an electron capture detector (Carlo Erba Strumentazione HRGC 5160 with an ECD 400, Milan, Italy). Analytical blanks were between 10 and 100 fM for a given PCB congener (in Table 2) per total sample; hence at a station like BATS where 657 L was filtered, this implies a blank concentration between 0.01 and 0.1 fM for each congener. In all cases, the specific congener blank was at least a factor of 3 lower than any concentration reported here. Recoveries for PCB standards for both samples and blanks were 50–105%, and reported data are corrected for these procedural internal standard yields. The precision of the analysis, expressed as the relative standard deviation of the internal standard yields, was about ±20%.

^{238}U and ^{234}Th Sampling and Analysis. Collection of ^{238}U and ^{234}Th samples was performed at the same time and using similar volumes as for HOCs but using a second system, optimized for trace metal and radionuclide sampling. The analytical protocols for these radionuclides have been described previously (37, 56). Briefly, seawater was pumped peristaltically through plastic tubing, and samples were extracted in-line through a 1-μm filter and two serially coupled MnO_2-impregnated adsorbers (57). Combusted filters and adsorbers were dissolved in concentrated acid and spiked with ^{230}Th yield tracer prior to standard radiochemical purification procedures (56). Samples for ^{234}Th were counted 4–5 times with weekly intervals on low background β-detectors. Thorium recoveries, from ^{230}Th quantification by α-counting spectrometry (56), were in the range 75–100%. ^{238}U activities were estimated from salinity based on the conservative relationship between ^{238}U and salinity in seawater (58). This constancy was verified for both coastal (37) and open ocean (36) regions of this study by direct measurement of ^{238}U abundance with isotope-dilution mass spectrometry.

Results and Discussion

Description of Ocean Scavenging Regimes Using ^{238}U and ^{234}Th. The magnitude of the radioactive disequilibrium between ^{238}U and ^{234}Th is an excellent indicator of the chemical scavenging intensity of different marine regimes. This is illustrated by the range of ^{234}Th/^{238}U activity ratios (= 100% at radioactive equilibrium) found in this study. This ratio ranged from 5% at the innermost station in 1993 to more than 85% in the pelagic Sargasso Sea (Table 1). The trend of decreasing ^{234}Th/^{238}U ratios when approaching more particle-

rich coastal waters (Table 1) has been commonly observed in previous studies (e.g., 31 and 33). The fraction of total ^{234}Th that was found in the particulate fraction increased closer to shore (Table 1). Using eq 2, we calculated first-order settling rate constants for ^{234}Th-carrying gravitoids (Table 1). These removal rate constants correspond to ^{234}Th particulate residence times in the surface ocean of one to a few days in coastal waters and two weeks or more in the open ocean locations.

Abundances of PCB Congeners in Surface Ocean Particles. The particulate concentrations of several common PCB congeners decreased from femtomolar to attomolar levels from coastal to pelagic surface seawater (Table 2). Our data agreed well with the limited congener-specific particulate PCB data available from similar regimes. The most relevant data sets may be those for the North and Baltic Seas (59, 60). Although those investigators used a coarser filter (GF/C; ≈1.2 μm) than our GF/F (≈0.7 μm), our data for particulate PCB 52 of 6–20 fM in coastal and shelf samples are within the wide concentration range found in waters north of continental Europe (about 1–100 fM PCB 52; refs 59 and 60). Likewise, in the early 1980s, particulate (>0.7 μm) concentrations of PCB 52 in western Lake Superior were 60 fM (61). Particulate (GF/C) concentrations of PCB 128 in southern regions of the North Sea and in the Baltic Proper were reported to be in the range 0.3–3 fM, with values of 10 fM and higher in nearshore waters (59, 60). We found for this same congener a range of 1–3 fM in coastal and shelf particle fractions and as low as 0.17 fM in the open ocean (Table 2). This pelagic value may be contrasted with an unfiltered PCB 128 concentration of 1.4 fM in waters from 250 m depth at 47° N 20° W in the northeast Atlantic (24).

Particulate PCB concentrations were higher at our innermost station (station 93-4) during gale-force winds in 1993 as compared to the calmer and more typical conditions in 1994 (station 94-4; Table 2). This was likely a result of resuspension of underlying bottom sediments (water depth 8 m) known to contain elevated levels of PCBs at this site (62). Such a scenario is further supported by higher POC in 1993 (520 μg/L) than a year later (150 μg/L).

Using either the 1993 or 1994 coastal data sets (for stations 4 and 2) as a nearshore end-member, we found that the heavier PCBs exhibited a more rapid decrease in their particulate concentrations with increasing distance from the continental source than the less chlorinated congeners. Particulate concentrations of tetrachlorinated congeners (i.e., 52, 44, and 66) were relatively constant over continental shelf-length scales and were only a factor of 6 lower at the pelagic site (Table 2). In contrast, the particulate levels of octachlorinated congeners 199 and 194 both decreased sharply across the shelf and were a factor of 40 lower at the pelagic station relative to 1994 coastal values.

PCB Fluxes. Surface ocean export fluxes decreased with increasing distance offshore for all congeners (Figure 1). However, this drop off was more pronounced for the more particle-reactive congeners. While the flux of the tetrachlorinated congener 52 only decreased from 40 pmol m^{-2} d^{-1} in the four coastal samples to 2 pmol m^{-2} d^{-1} at the pelagic site (factor of 20 over 1600 km), the octachlorinated congener 194 decreased from 4 to 0.03 pmol m^{-2} d^{-1} (factor of 130) over the same distance (Figure 1). These data indicate that smaller congeners exist in the vapor phase in air to a larger extent and therefore may be transported longer distances through the atmosphere. Thus, the less-chlorinated congeners may consitute a larger portion of "total PCB" fluxes in regions far from their sources, and aggregate parameters such as [ΣPCB] will reflect different compositions in near-source versus distant locales.

The ^{234}Th-derived direct estimates of PCB export from the mixed surface layer may be compared with PCB fluxes obtained from ^{210}Pb-dated sediment cores available for
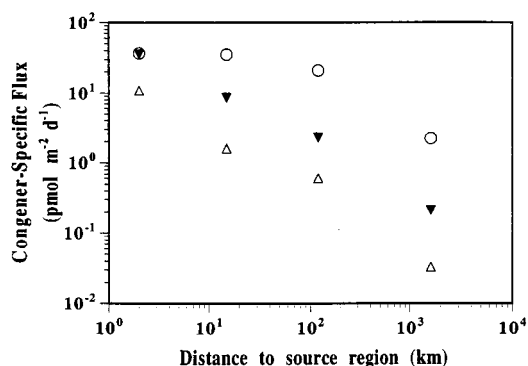
FIGURE 1. Vertical fluxes into the subsurface ocean of three PCB congeners over coastal to pelagic regimes of the western North Atlantic Ocean. (open circles, tetrachlorobiphenyl congener 52; filled inverted triangles, hexachlorobiphenyl congener 128; open triangles, octachlorobiphenyl congener 194). Fluxes were estimated from eq 3, using the geometric mean of the data in Tables 1 and 2 for each regime (i.e., 93-4 and 94-4 for nearshore, 93-2 and 94-2 for coastal, and 94-1 and 94-7 for continental shelf).
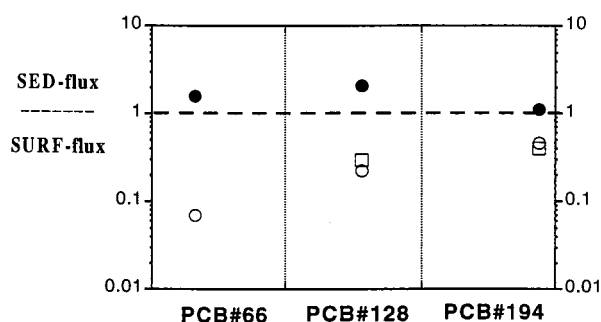

FIGURE 2. Comparison of PCB fluxes deposited in marine sediments versus fluxes deduced from ^{234}Th-derived export from the overlying surface ocean. The effect of congener-specific particle reactivity and water column depth on this ratio is illustrated using three different congeners at three Gulf of Maine stations of different depths: station 94-4 using two-dimensional flux model (37) at this nearshore station for this vertical flux comparison (filled circles, 8 m deep, sedimentation rate 3700 g dw m^{-2} yr^{-1}, [PCB 66] = 1.5 ng/g dw, [PCB 128] = 0.48 ng/g dw, and [PCB 194] = 0.25 ng/g dw); station 94-2 (open squares, 40 m, 1200 g dw m^{-2} yr^{-1}, [PCB 66] = not quantified, [PCB 128] = 0.049 ng/g dw, and [PCB 194] = 0.042 ng/g dw); and station 94-1 (open circles, 275 m, 1600 g dw m^{-2} yr^{-1}, [PCB 66] = 0.53 ng/g dw, [PCB 128] = 0.058 ng/g dw, and [PCB 194] = 0.036 ng/g dw). Further details about the derivation of the sedimentation rates are presented elsewhere (76).

stations 4, 2, and 1 using methods discussed in detail previously (29). The ratio of sediment PCB import fluxes to ^{234}Th-derived surface ocean export fluxes decreased both with depth of the water columns and with aqueous solubility of the congeners (Figure 2). The sediment and surface ocean fluxes of PCB 194 were equal at station 4, while the sediment fluxes were a factor of 2−3 smaller at the offshore stations 2 and 1. Sediment import for PCB 128 was twice the surface water export flux at station 4, but the bottom accumulation of PCB 128 was only one-third at station 2 and nearly 5 times smaller than the ^{234}Th-derived flux at station 1. The effect was even larger for the more soluble PCB 66 (PCB 52 was not quantified in the sediments), which showed about equal fluxes at station 4 but 15 times lower sediment import fluxes than surface ocean export fluxes through the deeper water column at station 1.

These trends suggest that the fingerprints and magnitudes of bottom sediment import fluxes are different from the surface ocean export fluxes as a result of particle dissolution and preferential desorption of more soluble congeners during settling or resuspension (10). These water column processes

would likely have an even larger effect in the pelagic ocean. In the Gulf of Maine, the compounds that became solubilized during settling are likely to become sequestered by the coastal sediments through "boundary scavenging" processes (37, 64) or to be advected out of the Gulf with the subpycnocline waters exiting through the Great South Channel. PCBs thus carried into intermediate Atlantic Ocean waters become isolated from the atmosphere for decadal to century-long periods.

Our ^{234}Th-derived export fluxes of PCBs may also be compared with previously reported congener-specific flux estimates. Panshin and Hites (7) used Junge's law to estimate atmospheric fluxes to the surface ocean in the same pelagic region (on nearby Bermuda) as our station BATS and at the same time (in 1993). They found PCB 52 fluxes of 6.1 pmol m^{-2} d^{-1} and PCB 194 fluxes of 0.036 pmol m^{-2} d^{-1}. Their calculated atmospheric flux of the tetrachlorinated congener (no. 52) was 3 times larger than our estimate of vertical removal, while the atmospheric deposition and fluxes into the ocean interior of the much less volatile octachlorinated congener (no. 194) were equal in the two studies.

At another site near Bermuda, Knap and co-workers (65) measured PCB fluxes into a 3200-m sediment trap between 1978 and 1980. They reported mean fluxes of PCB 52 and PCB 128 of 0.8 and 0.03 pmol m^{-2} d^{-1}, respectively. Obviously, these deep trap fluxes are expected to be much smaller than ^{234}Th-derived surface fluxes due to the generally decreasing flux of sinking particles with depth (49). To adjust these 3200 m deep ocean PCB fluxes for particulate organic matter degradation and associated PCB dissolution during settling, we scaled these deep PCB fluxes to the relative decrease in the OC flux from the surface waters to the OC flux in the deep trap. We feel that this is a reasonable approach as POC governs the particle affinity of PCBs and since Knap and co-workers observed a linear correlation between sedimenting particulate PCB and POC. To estimate the surface ocean OC flux, we used our POC value (29 μg/L) in place of [PCB$_{part}$] in eq 3. We thus obtain a surface ocean OC export of 36 mg m^{-2} d^{-1}, which is in good agreement with the mean ^{234}Th-derived OC export for this site of 31 mg m^{-2} d^{-1} found in a multi-year study (range 10−70 mg m^{-2} d^{-1}; ref 38). The ratio of our surface OC export (36 mg m^{-2} d^{-1}) and the deep ocean OC flux of Knap et al. (1.4 mg m^{-2} d^{-1}) was used to scale their observed deep trap flux of PCB 52 (0.8 pmol m^{-2} d^{-1}) and PCB 128 (0.03 pmol m^{-2} d^{-1}). From this, we estimate a surface ocean export flux in the late 1970s for congener 52 of 20 pmol m^{-2} d^{-1} and for congener 128 of 0.8 pmol m^{-2} d^{-1}. These estimates are up to an order of magnitude greater than what we observed in 1993 (2 and 0.2 pmol m^{-2} d^{-1} for PCB 52 and PCB 128, respectively). This decrease is consistent with the declining PCB fluxes seen for these and other PCB congeners over the same time period at other locations (16, 66, 67).

Sediment trap fluxes of PCB 52 reported for intermediate depths (250−750 m) in the central SW Mediterranean Sea were 1.5−3 pmol m^{-2} d^{-1} in 1992 (68), similar to our pelagic surface fluxes. Shallow (50 m) sediment trap fluxes in the NW Mediterranean in 1985−1986 for PCB 52 averaged 40 pmol m^{-2} d^{-1} (28). However, it should be borne in mind that such shallow trap fluxes may be inaccurate (47). Bottom sediment fluxes 1 decade later in the same region were 3 pmol m^{-2} d^{-1} for PCB 52 and 1.3 pmol m^{-2} d^{-1} for PCB 128 (69). These fluxes are somewhat lower than our continental shelf fluxes (21 and 2.3 pmol m^{-2} d^{-1}, respectively), which again may reflect incomplete transfer into the underlying sediments of material exported from the surface ocean. Sediment fluxes for PCB 52 of similar magnitudes have been reported for mid-1980s material in the Baltic Sea (67) and Lake Superior (70). Thus, it appears that the PCB fluxes we find using k_{settle} from ^{238}U−^{234}Th disequilibrium are consistent with other PCB flux observations.
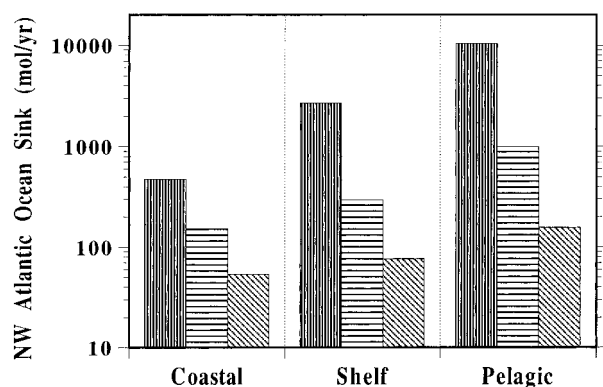
FIGURE 3. Receptor-based estimates of congener-specific ocean PCB sinks in coastal zone (<20 km), the remaining continental shelf, and the downwind portion of pelagic western North Atlantic Ocean off northeastern United States. Vertical hatched bars represent the area-integrated sinks of PCB 52, horizontal hatched bars are for congener 128, and diagonal hatched bars are the estimates for congener 194.

The Northwestern Atlantic Ocean PCB Sink. One of the largest obstacles to developing a global mass balance for PCBs has been the lack of reliable oceanic fluxes. The ^{234}Th-derived surface ocean export fluxes reported here provide an opportunity to estimate the magnitude of the western North Atlantic Ocean as a long-term repository of PCBs. We extrapolated our PCB fluxes following methods previously developed for PAHs in this region (29). Briefly, since transport on oceanic scales are considered, the entire northeastern U.S. seaboard is treated as a line source (length 1600 km). The geometric mean fluxes at stations 4 and 2 are applied to a coastal region 20 km wide (3.2×10^4 km^2), based on characteristic fallout patterns observed for semivolatile pollutants believed to be associated with large aerosols (e.g., refs 29 and 71). The area of the remaining northeastern continental shelf is 3.5×10^5 km^2 (72). The pelagic portion of the western North Atlantic Ocean is assumed to be predominantly affected by the westerly transport of pollutants from the United States and is treated as a 160° sector of a circle extending half-way across to Europe (1.3×10^7 km^2) and has our station BATS at a representative central location.

Based on our limited data set, the per unit area PCB fluxes appear to be larger closer to the continent (Figure 1). However, extrapolating these same limited data, assuming they are representative of their respective regions, we find that the area-integrated sinks for the deep pelagic ocean are quantitatively much more important for all congeners than sinks into more nearshore waters (Figure 3). Using the ^{234}Th-derived fluxes, we estimate that 14 000 mol yr^{-1} PCB 52 were sequestered in subsurface waters of the northwestern Atlantic Ocean in 1993, with 75% of the sink being in the pelagic sector, 20% over the continental shelf, and only 5% in the 20 km strip of ocean closest to the continental U.S. source. In contrast, of the 290 mol of PCB 194 removed annually to the same regions, roughly half was exported to the open ocean, 25% to the shelf, and 20% in the coastal section.

Such fractionation patterns contain information about the processes that govern the environmental dispersal of these compounds. For example, transformations of PCBs by vapor-phase atmospheric reactions with hydroxyl radicals may be a significant sink for some congeners in the global PCB mass balance (73, 74). The hydroxyl radical reaction rates generally decrease with increasing chlorination number. If atmospheric reactions with ·OH were important, one should expect a relative enrichment of more highly chlorinated congeners in "aged" samples farther removed from the continental source. On the other hand, the tendency to sorb to atmospheric or aquatic particles, and hence to be removed on settling particles, is directly related to each congener's degree of

chlorination (e.g., ref 40). Thus, if atmospheric washout and export from the surface ocean were the predominant removal mechanisms, one would expect a relative enrichment of the less chlorinated congeners in samples farther removed from the continental source. Our results show that the concentrations of the less chlorinated congeners decrease less sharply than those of the larger PCBs with increasing distance from the continent; therefore, a sink that favors removal of larger PCBs must be dominating. Hence, the congener patterns along this ocean transect suggest that, during the atmospheric transport of an air parcel from the northeast United States to the pelagic North Atlantic, entrainment of PCBs into the surface ocean followed by scavenging on particles settling into the ocean interior is a quantitatively more important sink than hydroxyl radical reactions even for less chlorinated congeners. Thus, the atmospheric reaction of PCB 52 with hydroxyl radical above the western North Atlantic must be significantly less than 14 000 mol yr^{-1}.

We may contrast our estimated North Atlantic Ocean sink with other congener-specific sink estimates. Tolosa et al. (69) found that 180 (PCB 52) and 140 mol/yr (PCB 128) were buried in the bottom sediments of the NW Mediterranean Sea. Significant work on the PCB cycling in the Laurentian Great Lakes has been performed over the past 2 decades. A comparison with that data is complicated since our three target congeners have commonly not been reported (e.g., refs 8, 10, and 12) and recent mass balance calculations have been reported as a "total PCB" parameter (e.g., refs 4 and 16). If we assume that PCB 52 is 4% of total PCB (69, 75) in the Great Lakes sediments, we can estimate that approximately 20 mol/yr of this congener was buried annually during the mid-1980s in Lake Superior (16) and 200 mol/yr was buried in Lake Michigan during the early 1990s (4). This comparison suggests that the vast expanses of the western North Atlantic Ocean are a significantly greater sink for PCBs than either the Laurentian Great Lakes or the western Mediterranean Sea. It should be emphasized that there are large uncertainties associated with extrapolating this first set of surface ocean export fluxes to the whole western North Atlantic Ocean. Nevertheless, these congener-specific results show the importance of attempting to constrain the magnitude of this oceanic sink in order to understand the global dispersal of semivolatile xenobiotic compounds such as PCBs.

It is not simple to determine whether our estimated PCB fluxes into the long-term North Atlantic Ocean repository are significant on a global scale since very little is known about what fraction of each PCB is presently cycling through the contemporary environment. Of the total U.S. PCB production of 6×10^8 kg, it has been estimated that approximately 15% entered the contemporary environment (18). In an effort to obtain a congener-specific source estimate, one may use the relative contribution of PCB 52, 128, and 194 in a 1:1:1 mixture of the most common U.S. industrial PCB mixtures Arochlors 1242, 1254, and 1260 (75). This results in a gross U.S. release estimate for these three congeners of 1×10^7 mol (PCB 52), 4×10^6 mol (PCB 128), and 8×10^5 mol (PCB 194). The present annual fluxes into the North Atlantic Ocean correspond to roughly 0.1% of the source inventory for PCB 52 and less than 0.01% for PCB 194. However, as we have discussed above, it is reasonable to expect that these fluxes were an order of magnitude larger 15 years ago, and they were probably even larger throughout the 1960s and 1970s. This suggests that a significant fraction of the PCBs released in the United States indeed may have found their way into the North Atlantic Ocean by this time. Clearly, further studies on fluxes and water column inventories of PCBs in the North Atlantic is warranted.

The ^{234}Th-coupled HOC ocean flux approach utilized in this study could fill the considerable absence of reliable ocean sink estimates that exist for many hydrophobic organic contaminants. This information is required to make progress

toward estimates of global HOC mass balances. In particular, this methodology may be effective for quantifying a first-order particle removal rate (k_{settle}) applicable to any substance that associates with the same solids as ^{234}Th. Moreover, investigations of environmental fractionation patterns between individual congeners—like the pattern we report indicating the predominance of ocean scavenging over hydroxyl radical transformations as a PCB sink—may enable us to deduce governing mechanisms affecting chemical fates.

Acknowledgments

Literature Cited

(1) *Polychlorinated Biphenyls (PCBs): Mammalian and Environmental Toxicology;* Safe, S., Hutzinger O., Eds.; Springer-Verlag; Berlin, 1987.

(2) Giesy, J. P., Ludwig, J. P.; Tillitt, D. E. *Environ. Sci. Technol.* **1994**, *28*, 128.

(3) Jones, K. C.; Sanders, G.; Wild, S. R.; Burnett, V.; Johnston, A. E. *Nature* **1992**, *356*, 137.

(4) Pearson, R. F.; Hornbuckle, K. C.; Eisenreich, S. J.; Swackhamer, D. L. *Environ. Sci. Technol.* **1996**, *30*, 1429.

(5) Loganathan, B. G.; Tanabe, S.; Hidaka, Y.; Kawano, M.; Hidaka, H.; Tatsukawa, R. *Environ. Pollut.* **1993**, *81*, 31.

(6) Baker, J. E.; Eisenreich, S. J. *Environ. Sci. Technol.* **1990**, *24*, 342.

(7) Panshin, S. Y.; Hites, R. A. *Environ. Sci. Technol.* **1994**, *28*, 2001.

(8) Eisenreich, S. J.; Looney, B. B.; Thornton, J. D. *Environ. Sci. Technol.* **1981**, *15,* 30.

(9) Baker, J. E.; Eisenreich, S. J.; Johnson, T. C.; Halfman, B. M. *Environ. Sci. Technol.* **1985**, *19*, 854.

(10) Baker, J. E.; Eisenreich, S. J.; Eadie, B. J. *Environ. Sci. Technol.* **1991**, *25*, 500.

(11) Howdshell, M. J.; Hites, R. A. *Environ. Sci. Technol.* **1994**, *28*, 1691.

(12) Hornbuckle, K. C.; Jeremiason, J. D.; Sweet, C. W.; Eisenreich, S. J. *Environ. Sci. Technol.* **1994**, *28*, 1491.

(13) McConnell, L. L.; Kucklick, J. R.; Bidleman, T. R.; Ivanov, G. P.; Chernyak, S. M. *Environ. Sci. Technol.* **1996**, *30*, 2975.

(14) Sanders, G.; Jones, K. C.; Hamilton-Taylor, J. *Environ. Sci. Technol.* **1992**, *26*, 1815.

(15) Axelman, J.; Bandh, C.; Broman, D.; Carman, R.; Jonsson, P.; Larsson, H.; Linder, H.; Näf, C.; Pettersen, H. *Mar. Freshwater Res.* **1995**, *46*, 137.

(16) Jeremiason, J. F.; Hornbuckle, K. C.; Eisenreich, S. J. *Environ. Sci. Technol.* **1994**, *28*, 903−914.

(17) Axelman, J.; Näf, C.; Bandh, C.; Ishaq, R.; Pettersen, H.; Zebühr, Y.; Broman, D. In *A Systems Analysis of the Changing Baltic Sea*; Wulff, F., Rahm, L., Larsson, P., Eds.; Springer-Verlag: Berlin, in press.

(18) National Academy of Sciences. *Polychlorinated Biphenyls*; U.S. NAS: Washington, DC, 1979.

(19) Miller, S. *Environ. Sci. Technol.* **1982**, *16*, 98.

(20) Tanabe, S. *Environ. Pollut.* **1988**, *50*, 5.

(21) Alcock, R. E.; Johnston, A. E.; McGrath, S. P.; Berrow, M. L.; Jones, K. C. *Environ. Sci. Technol.* **1993**, *27*, 1918.

(22) Jones, K. C.; Duarte-Davidson, R.; Cawse, P. A. *Environ. Sci. Technol.* **1995**, *29*, 53.

(23) Harvey, G. R.; Steinhauer, W. G. *J. Mar. Res.* **1976**, *34*, 562.

(24) Schulz, D. E.; Petrick, G.; Duinker, J. C. *Mar. Pollut. Bull.* **1988**, *19*, 526.

(25) DeLappe, B. W.; Risebrough, R. W.; Walker, W. *Can. J. Fish. Aquat. Sci.* **1983**, *40* (S2), 322.

(26) Farrington, J. W.; Westall, J. In *The Role of the Oceans as a Waste Disposal Option*; Kullenberg, G., Ed.; Reidel: Dortmund, 1986.

(27) Petrick, G.; Schulz-Bull, D. E.; Martens, Scholz, K.; Duinker, J. C. *Mar. Chem.* **1996**, *54*, 97.

(28) Fowler, S. W.; Ballestra, S.; Villeneuve, J.-P. *Cont. Shelf Res.* **1990**, *10*, 1005.

(29) Gustafsson, Ö.; Gschwend, P. M.; Buesseler, K. O. *Mar. Chem.* **1997**, *57*, 11.

(30) Broecker, W. S.; Peng, T.-H. *Tellus* **1974**, *26*, 21.

(31) Moran, S. B.; Buesseler, K. O. *J. Mar. Res.* **1993**, *51*, 893.

(32) Anderson, R. F. *Geochim. Cosmochim. Acta* **1982**, *46*, 1293.

(33) Bhat, S. G.; Krishnaswami, S.; Lal, D.; Rama; Moore, W. S. *Earth Planet. Sci. Lett.* **1969**, *5*, 483.

(34) Coale, K. H.; Bruland, K. W. *Limnol. Oceanogr.* **1985**, *30*, 22.

(35) Buesseler, K. O.; Bacon, M. P.; Cochran, J. K.; Livingston, H. D. *Deep-Sea Res.* **1992**, *39*, 1115.

(36) Buesseler, K. O.; Michaels, A. F.; Siegel, D. A.; Knap, A. H. *Global Biogeochem. Cycles* **1994**, *8*, 179.

(37) Gustafsson, Ö.; Buesseler, K. O.; Geyer, W. R.; Moran, S. B.; Gschwend, P. M. *Cont. Shelf Res.* Submitted for publication.

(38) Buesseler, K. O. *Global Biogeochem. Cycles* In press.

(39) Gustafsson, Ö.; Gschwend, P. M. *Limnol. Oceanogr.* **1997**, *42*, 519.

(40) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: New York, 1993.

(41) Fowler, S. W.; Knauer, G. A. *Prog. Oceanogr.* **1986**, *16*, 147.

(42) Farley, K. J.; Morel, F. M. M. *Environ. Sci. Technol.* **1986**, *20*, 187.

(43) Alldredge, A. L.; Silver, M. W. *Prog. Oceanogr.* **1988**, *20*, 41.

(44) Stolzenbach, K. D. *Deep-Sea Res. I* **1993**, *40*,359.

(45) Gardner, W. D. *J. Mar. Res.* **1980**, *38*, 41.

(46) Knauer, G.; Asper, V. *Sediment Trap Technology and Sampling*; U.S. GOFS Planning Report Number 10, 1989.

(47) Buesseler, K. O. *Nature* **1991**, *353*, 420.

(48) Bacon, M. P.; Anderson, R. F. *J. Geophys. Res.* **1982**, *87*, 2045.

(49) Martin, J. H.; Knauer, G. A.; Karl, D. M.; Broenkow, W. W. *Deep-Sea Res.* **1987**, *34*, 267.

(50) Berner, R. A. *Early Diagenesis: A Theoretical Approach*; Princeton, University Press: Princeton, NJ, 1980.

(51) Wong, C. S.; Sanders, G.; Engstrom, D. T.; Swackhamer, D. L.; Eisenreich, S. J. *Environ. Sci. Technol.* **1995**, *29*, 2661.

(52) Gustafsson, Ö.; Buesseler, K. O.; Gschwend, P. M. *Mar. Chem.* **1996**, *55*, 93.

(53) Gustafsson, Ö.; Gschwend, P. M. In *The Application of Molecular Markers in Environmental Geochemistry*; Eganhouse, R. B., Ed.; American Chemical Society Symposium Series; ACS: Washington, DC, 1997; Chapter 24.

(54) Takada, H.; Ishiwatari, R. *J. Chromatogr.* **1985**, *346*, 281.

(55) Schulz, D. E.; Petrick, G.; Duinker, J. C. *Environ. Sci. Technol.* **1989**, *23*, 852.

(56) Buesseler, K. O.; Cochran, J. K.; Bacon, M. P.; Livingston, H. D.; Casso, A.; Hirschberg, D.; Hartman, M. C.; Fleer, A. P. *Deep-Sea Res. I* **1992**, *39*, 1103.

(57) Hartman, M. C.; Buesseler, K. O. Woods Hole Oceanographic Institution Technical Report WHOI-94-15. 1994; 16 pp.

(58) Chen, J. H.; Edwards, R. L.; Wasserburg, G. J. *Earth Planet. Sci. Lett.* **1986**, *80*, 241.

(59) Schulz-Bull, D. E.; Petrick, G.; Duinker, J. C. *Mar. Chem.* **1991**, *36*, 365.

(60) Schulz-Bull, D. E.; Petrick, G.; Kannan, N.; Duinker, J. C. *Mar. Chem.* **1995**, *48*, 245.

(61) Baker, J. E.; Capel, S. J.; Eisenreich, S. J. *Environ. Sci. Technol.* **1986**, *20*, 1136.

(62) Kennicutt, M. C., II; Wade, T. L.; Presley, B. J.; Requejo, A. G.; Brooks, J. M.; Denoux, G. J. *Environ. Sci. Technol.* **1994**, *28*, 1.

(63) Hawker, D. W.; Connell, D. W. *Environ. Sci. Technol.* **1988**, *22*, 382.

(64) Bacon, M. P. *Philos. Trans. R. Soc. (London)* **1988**, *87*, 2045.

(65) Knap, A. H.; Binkley, K. S.; Deuser, W. G. *Nature* **1986**, *319*, 572.

(66) Lead, W. A.; Steinnes, E.; Jones K. C. *Environ. Sci. Technol.* **1996**, *30*, 524.

(67) Kjeller, L.-O.; Rappe, C. *Environ. Sci. Technol.* **1995**, *29*, 346.

(68) Dachs, J.; Bayona, J. M.; Fowler, S. W.; Miquel, J.-C.; Albaiges, J. *Mar. Chem.* **1996**, *52*, 75.

(69) Tolosa, I.; Bayona, J. M.; Albaigés, J. *Environ. Sci. Technol.* **1996**, *30*, 2495.

(70) Swackhamer, D. L.; McVeety, B. D.; Hites, R. A. *Environ. Sci. Technol.* **1988**, *22,* 664.

(71) Näf, C.; Broman, D.; Pettersen, H.; Rolff, C.; Zebühr, Y. *Environ. Sci. Technol.* **1992**, *26*, 1444.

(72) Buesseler, K. O.; Livingston, H. D.; Sholkovitz, E. R. *Earth Planet. Sci. Lett.* **1985/86**, *76*, 10.

(73) Atkinson, R. *Environ. Sci. Technol.* **1987**, *21*, 305.

(74) Anderson, P. N.; Hites, R. A. *Environ. Sci. Technol.* **1996**, *30*, 1756.

(75) Eganhouse, R. P.; Gossett, R. W. *Anal. Chem.* **1991**, *63*, 2130.
(76) Gustafsson, Ö.; Gschwend, P. M. *Geochim. Cosmochim. Acta* In press.