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Fate of Linear Alkylbenzenes Released to the Coastal Environment near Boston Harbor

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Linear alkylbenzenes (LABs) were used to assess the fates of hydrophobic organic compounds (HOCs) released to a large urban harbor and the adjoining offshore waters. We found that particulate concentrations of the individual C_{12} LAB isomers in 1996 summertime surface waters decreased from 1 pM in Boston Harbor to 20−200 fM in coastal Massachusetts and Cape Cod Bays. Levels fell to only a few fM in offshore Gulf of Maine locations. These observations were consistent with municipal wastewater in Boston Harbor as the predominant input followed by dispersal via known circulation patterns in this region. Phase-dependent removal rate coefficients for flushing, vertical scavenging, volatilization, photodegradation, and biodegradation of individual LAB isomers were constrained from literature, field observations, and laboratory experiments and combined with estimates of wastewater release rates into a predictive 3-box model. Vertical scavenging, biodegradation, and flushing were predicted to be the most important fate processes for C_{12} LABs in the Boston Harbor−MA Bay−Cape Cod Bay flow system with about 1% of the harbor releases "surviving" passage. For HOCs such as the relatively bio-recalcitrant LAB, 6-phenyldodecane, it appears that we are at present able to predict the coastal fate of harbor-introduced HOCs in this system within a factor of 2. Contrary to expectations from biodegradation experiments, the ratio of internal-to-external (I/E) LAB isomers decreased offshore in both water and sediment samples, suggesting we are "missing" an important process affecting LAB fates.

Introduction

Ocean disposal of industrial and domestic wastes has created a legacy of severely polluted harbors and coastal waterways (*1*−*3*). To evaluate the potential for adverse impacts, we need to assess the environmental fates of the chemicals in those wastes. Such assessments enable us to anticipate the exposures of organisms and ecosystems to those substances.

Here, we examine the situation for some hydrophobic organic compounds (HOCs) released to Boston Harbor, a historically polluted harbor in the USA. Additionally, we follow these compounds into the adjoining waters of Massachusetts Bay, Cape Cod Bay, and the larger Gulf of Maine, generally considered one of the most pristine coastal regions along the eastern US seaboard (Figure 1). Several previous studies have assessed organic pollutant inputs to Boston Harbor (e.g., *4*−*7*). These and other investigations have concluded that the major source of many HOCs to Boston Harbor has been municipal wastewater. Until recently, these effluents were discharged from two antiquated primary treatment plants; a new primary treatment facility handling all the wastewater began operation in early 1995, but the legally mandated secondary treatment was not in full use until July 1998.

It is a challenge to ascertain the contribution of wastewater-derived substances to the total exposure for many HOCs in settings such as Massachusetts Bays and the Gulf of Maine. HOCs such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) have several potentially important entry routes to the coastal ocean, in addition to municipal wastewater disposal. Thus, the distributions of these HOCs do not reflect the effects of wastewater inputs alone. Ideal tracers of the HOCs entering via wastewater should be uniquely found in this input, should be relatively persistent in the marine environment, and should exhibit a range of physicochemical properties that allow environmental behaviors of similar compounds to be inferred (*8*−*9*). The long-chain linear alkylbenzenes (LABs) have been proposed as such molecular tracers for wastewater-derived hydrophobic contaminants in coastal waters (e.g., refs *8* and *10*). Consisting of a suite of 26 secondary phenylalkanes with chain lengths ranging from 10 to 14 carbon atoms, commercial LAB mixtures are principally used as raw material in the production of the widely used anionic surfactants, linear alkylbenzene sulfonates (LASs). During sulfonation, 1 to 3% of LABs remain unreacted (*11*). Thus, LABs remain as a trace residue in cleaners and detergents, and these HOCs enter the aquatic environment wherever LASs are being used and released. Generally, such surfactants and the associated LABs are discharged to wastewater. Many previous workers have examined the fate of LABs in coastal marine environments (e.g., refs *7*, *8*, *10*, and *12*−*18*). Here, we use LABs as source-specific molecular markers of pollution from a large urban harbor to assess a box model approach for understanding the fate of HOCs in an urban harbor and the adjoining offshore waters.

Since the ability of a chemical to participate in certain processes is dictated by its phase associations, the distribution of HOCs between dissolved, colloidal, and settling particle-sorbed species must be understood. Thus, mass balance models, considering these species, must be formulated. For example, the time-rate of change of the total concentration of an HOC in coastal seawater is the combined change exhibited by each species:

$$\frac{dC_t}{dt} = \frac{dC_d}{dt} + \frac{dC_c}{dt} + \frac{dC_p}{dt} = \frac{I_t}{V} + k_g\frac{C_a}{K'_H} - k_w C_t - f_w(k_g + k_{r,d})C_t - f_c(k_{r,c})C_t - f_p(k_s + k_{r,p})C_t \quad (1)$$

where C_t is the total concentration of the HOC of interest (mol m^{-3}), C_d is the concentration of the dissolved species (mol m^{-3}), C_c is the concentration of the colloid-bound species (mol m^{-3}), C_p is the concentration of settling particle-

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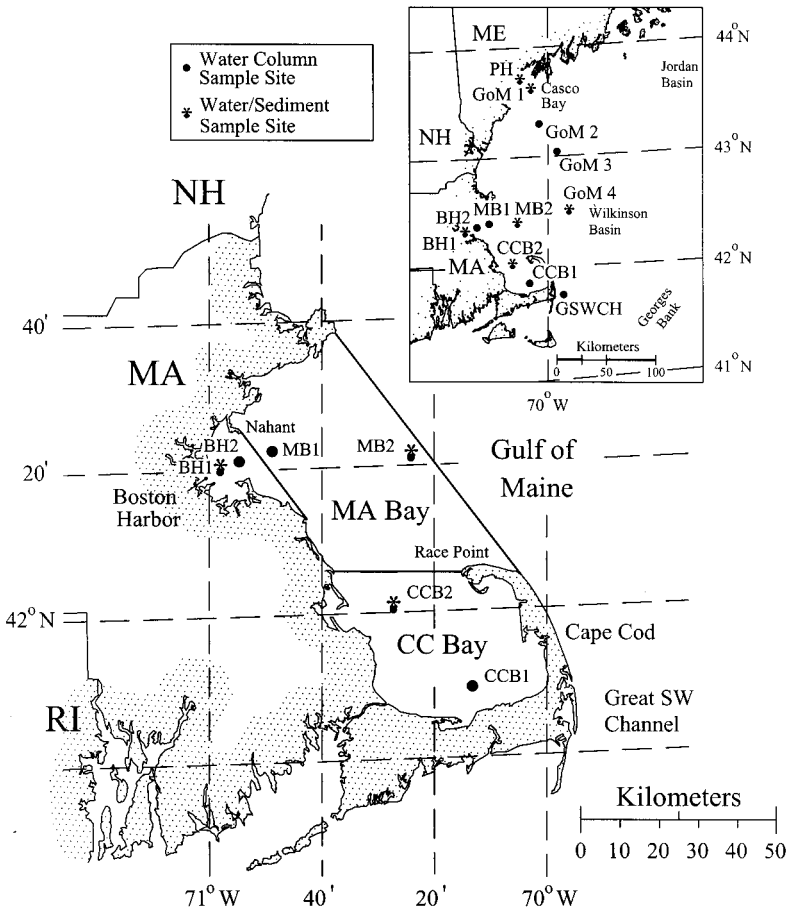

FIGURE 1. The study region in the Gulf of Maine with the region of Boston Harbor and adjoining Massachusetts and Cape Cod Bays enlarged. Filled circles denote water column stations while filled circles associated with a star mark locations where surface sediments were retrieved. The bold lines delineate the areal extents of the boxes in the mass balance model.

bound species (mol m^{-3}), V is the volume of the water body considered (m^3), I_t represents total inputs via discharges (mol), $k_g C_a/K'_H$ gives inputs from the atmosphere as the product of the air−water exchange coefficient k_g (m $year^{-1}$) and the concentration of the water at equilibrium with the atmosphere C_a/K'_H (mol m^{-3}), k_w reflects losses from the volume due to flushing ($year^{-1}$), $f_w(k_g + k_{r,d})$ quantifies the losses of the dissolved fraction (f_w; dimensionless), due to volatilization (k_g) and in situ homogeneous reactions here represented as the sum of rates of photolysis, biodegradation, and other reactions ($k_{r,d}$; $year^{-1}$), $f_c(k_{r,c})$ represents the losses of the colloidal fraction (f_c; dimensionless), due to in situ reactions ($k_{r,c}$; $year^{-1}$), and $f_p(k_s + k_{r,p})$ describes the losses of the fraction of HOCs bound to particles large enough to be collected on a GF/F filter ($\approx 0.7\ \mu$m), (f_p; dimensionless), due to settling (k_s; $year^{-1}$) and in situ solid-phase reactions ($k_{r,p}$; $year^{-1}$).

The fraction of each species that is lost can be estimated assuming that phase distribution equilibrium applies and using knowledge of each phase's abundance and the corresponding distribution coefficients. For example, the dissolved fraction is estimated to be

$$f_w = 1/(1 + r_{cw}K_{cw} + r_{sw}K_{sw}) \qquad (2)$$

where r_{cw} is the ratio of the mass of colloids-to-water volume (kg m^{-3}), K_{cw} is the colloid-water partition coefficient (m^3 kg^{-1}), r_{sw} is the ratio of the mass of settling solids-to-water volume (kg m^{-3}), and K_{sw} is the settling solid−water partition coefficient (m^3 kg^{-1}).

The mass balance and partitioning equations indicate the terms that are needed to predict HOC concentrations in coastal waters. In the subsequent sections, estimates will be developed of both the distribution of LABs among dissolved, colloidal and settling solids phases and the rates of the different processes affecting them. These parameters will be used to predict LAB concentrations for direct comparison with our measurements to test how well we are currently able to describe the behavior of HOCs in coastal waters. We stress that it is not our intent to adjust the model to fit our LAB data, but rather to (i) indicate how well we understand the key processes influencing HOCs in the coastal zone and (ii) identify where future efforts should be focused. Simultaneously "fitting" data for all the components of a co-introduced suite of substances such as the LABs should allow us to use fractionations of these mixtures to indicate the nature of any missing sources or sinks.

Materials and Methods

Study Area. Boston Harbor (BH) is tidally flushed, thereby exporting contaminants to the adjoining coastal regions of Massachusetts Bay (MB), Cape Cod Bay (CCB), and the larger Gulf of Maine (GoM) (Figure 1). Trajectories of drifters released in MB, just outside the mouth of BH, reveal a weak counterclockwise circulation with a distinct southward drift along the western shore into Cape Cod Bay (*19*). Generally, currents do not transport water from the outlet of BH to the northeast and directly into the open GoM Proper. After the flow slows in the lower reaches of CCB, drifter trajectories indicate that the water from this region follows an eastward and then northward flow along the Cape Cod peninsula. Subsequently, this water exits to the north and east around Race Point into the Georges Bank region and/or out of the Gulf of Maine system. Hence, the sequence of BH, MB, and CCB constitutes a "continuous flow system" that can be used

TABLE 1. Physicochemical Properties and Estimates of Phase Partitioning in Coastal Seawaters for LABs

	2-C_{12}	3-C_{12}	4-C_{12}	5-C_{12}	6-C_{12}	5-C_{11}
log K_{ow}[a]	8.19	8.10	8.07	8.01	8.01	7.45
log K_{POC} (L_w/kg_{POC})[b]	7.85	7.76	7.73	7.67	7.67	7.10
log $K_{D+C\ OC}$ ($L_w/kg_{D+C\ OC}$)[c]	6.28	6.21	6.18	6.14	6.14	5.68
Fraction Dissolved[d]						
BH	0.028	0.034	0.037	0.042	0.042	0.14
MB	0.066	0.079	0.084	0.095	0.095	0.066
CCB	0.12	0.14	0.15	0.16	0.17	0.12
GoM	0.076	0.092	0.098	0.11	0.11	0.30
Fraction Large-Particle Bound[d]						
BH	0.91	0.90	0.90	0.89	0.89	0.79
MB	0.78	0.77	0.76	0.75	0.75	0.78
CCB	0.66	0.64	0.63	0.61	0.61	0.66
GoM	0.78	0.76	0.76	0.74	0.74	0.56

[a] From ref *43*. [b] Estimated using relationship regressed with K_{ow} in ref *39*. [c] Estimated using relationship with K_{POC} in ref *33*. [d] Using DOC and POC shown in Table 3; note that calculated fraction dissolved does not include fraction colloidal.

to study the fates of wastewater-derived pollutants. In fact, Bothner and Buchholtz ten Brink (*20*) have observed anomalously high concentrations and inventories of another wastewater tracer, silver, in CCB sediments. In the vertical, two seasonal hydrographic regimes prevail. MB and CCB are well-mixed in the winter (Nov−March), while stratification is a dominant feature from May to October (*21*).

LAB Source Functions. The inputs of LABs to Boston Harbor were estimated as the product of effluent discharge times the measured LAB concentrations in monthly samples of the wastewater from the Deer Island and Nutt Island sewage treatment plants (*22*, *23*). Eganhouse and Sherblom (*7*) have shown that this municipal wastewater discharge overwhelmed combined sewer overflows as a source of LABs to Boston Harbor. The C_{12} LAB isomers contribute 34 ± 3% of the total LABs in Boston Harbor effluents (*22*, *24*). The internal-to-external isomer distribution [I/E is the ratio of internal to external isomers, (6+5)/(4+3+2); where the numbers refer to the position of the phenyl substitution for the different isomers, e.g., ref *13*] seen in BH wastewater (I/E = 0.86) is in the range found in commercial detergents (0.5−1.2, n = 10; unpublished results; Robert Eganhouse, United States Geological Survey, Reston, VA, personal communication, September 2000). Hence, to calculate the inputs of the individual LABs into Boston Harbor, we used the C_{12} isomer composition of a commercial detergent with LAB composition very similar to BH effluent (33% C_{12} LABs and I/E of 0.85; ref 24). Its C_{12} isomer composition as percentages of total LAB is 7.4, 7.9, 5.3, 5.9, and 6.8% by mass of the 6-, 5-, 4-, 3-, and 2-C_{12} LABs, respectively (Figure 3 in ref 24).

Field Sampling and Analysis. Since LABs are highly hydrophobic (Table 1), they should be largely associated with suspended solids in seawater. Hence, to measure these trace constituents, we filtered large volumes of seawater at a set of stations distributed throughout the BH−MB−CCB−GoM system (Figure 1). Sampling of surface seawater for trace organic compounds was performed during stratified conditions in July 1996 at two or more stations in each region. We have previously described our sampling system (*25*) and shipboard methodology aimed at minimizing both contamination and artificial sample fractionation (*26*). Briefly, water was pumped from the middle of the mixed layer 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 316 SS grade stainless steel tubing. The samples, ranging in size from 300 L at harbor stations to nearly 2000 L at the outermost station, were filtered at <20 psi in-line through a precombusted Whatman GF/F (≈ 0.7 μm) glass fiber filter in a 293-mm diameter stainless steel holder.

Sediment subcores for HOCs were obtained using a Sandia-Hessler MK-III box corer (*26*). In addition to the cores obtained on this cruise (at MB 2 and CCB 2; Figure 1), we also determined LABs in sediments from the mid-Gulf region and Wilkinson Basin collected in 1994 (*26*, *27*).

Determination of LABs. All glassware was cleaned in a multistep protocol, including using carefully selected detergent that does not contain LASs (Fisherbrand Versa-clean, Fisher, Pittsburgh, PA). We used chromic−sulfuric acid baths, followed by rinses in high-purity water (Vaponics Systems, Rockland, MA) and ultra-resi analyzed grade solvents (J. T. Baker Inc.) For LAB analysis, the sample filters or sediments were spiked with three LAB recovery surrogates (1-C_9, 1-C_{12}, and 1-C_{14}). All LAB standards were 97−99% pure and were used as purchased (Aldrich, Milwaukee, WI, and Johnson Matthey, Ward Hill, MA). The samples were placed in precleaned glass thimbles and were Soxhlet extracted for 48 h in a 9:1 methylene chloride/methanol mixture. After extracts were dried with anhydrous sodium sulfate, elemental sulfur was removed via activated copper (prepared according to ref *28*). Then the extracts were fractionated using a fully activated silica gel column (method modified from ref *29*). The resulting LAB-containing fraction was concentrated using either rotary evaporation or Kuderna-Danish evaporators. The LABs were separated and quantified with similar gas chromatography−mass spectrometry (GCMS) techniques described earlier for PAHs and PCBs (*26*, *30*). Signals for LABs were acquired in selected ion mode (SIM) at m/z 91 and 105. On-column injections of the final concentrates were amended with 1-C_{10}, 1-C_{11}, and 1-C_{13}-LABs as MS quantitation standards to determine the recoveries of the LAB recovery surrogates (1-C_9: 49 ± 17%, 1-C_{12}: 62 ± 21%, and 1-C_{14}: 78 ± 30%; where the uncertainty represents one standard deviation for observations made on 12 samples). Response factors of each individual LAB isomer were determined by analysis of a commercial LAB mixture (Alkylate 225; kindly provided by the Huntsman Chemicals Co., St. Louis, MO) whose congener composition had previously been determined by GC-FID analysis (*6*).

^{238}U and ^{234}Th in Seawater. The disequilibrium between the two natural radionuclides, ^{238}U (highly water soluble), and its radiogenic product, ^{234}Th (highly particle reactive), can be used to quantify the rate of removal of settling particulate matter from the surface ocean. Coupling this radioactive "tracer" of particle export to the particulate inventory of HOCs allows one to determine particle-mediated removal rate coefficients, k_s, suited to quantifying losses out of the surface ocean of organic pollutants sorbed to settling particles (*26*, *30*). Collection of ^{234}Th samples took place in parallel to LAB sampling. The protocols for sampling and subsequent radiochemical purification and counting techniques have been described in detail elsewhere (*31*, *32*).

"Dissolved plus Colloidal" and Particulate Organic Carbon. The organic carbon in the large particulate phase, referred to as POC, was quantified using a Perkin-Elmer 2400 CHN, following an acid-fuming step to remove inorganic carbon. Similarly, the filtrate ["dissolved + colloidal" organic carbon (D+C OC)] was determined in triplicate using a Shimadzu TOC-5000 high-temperature catalytic oxidation instrument following removal of dissolved inorganic carbon according to ref *25*.

Colloid Association Experiment. We used time-resolved fluorescence quenching to assess associations of hydrophobic organic compounds to seawater colloids without having to separate the dissolved and colloidal phases. Both artificial

seawater (low-carbon, 18 MΩ water, adjusted to pH 8.0 and ionic strength 0.7 M) and coastal seawater (GoM1; Figure 1) were amended with 1-methylperylene. This compound was selected as an HOC probe because of its high fluorescence quantum yield and a hydrophobicity (log K_{ow} = 6.8; ref *33*) near that of the C_{12} LABs. All fluorescence intensity and lifetime measurements were obtained with an ISS K2-Digital fluorometer (ISS Inc., Champaign, IL). Single-wavelength intensity data (406/442 nm; with a KV 418 high-band-pass emission filter) were acquired in photon-counting mode, using a photomultiplier tube cooled to −8 °C with an auxiliary Peltier system. The K2-Digital instrument utilizes the variable-frequency phase and modulation technique to obtain fluorescence lifetimes (*34*). For 1-methylperylene, excitation light was modulated over 16 logarithmically spaced frequencies in the range 2−200 MHz. Phase-shifts and demodulation factors were collected using a cross-correlation frequency of 80 Hz. Raleigh scatter from a freshly prepared aqueous glycogen solution was assigned a reference lifetime of 0 ns. The collected phase and modulation data were analyzed with ISS187 decay analysis software using a Marquardt-Levenburg least-squares minimization algorithm to derive estimates of lifetime distributions of different components. Further details on the experimental procedures, including system deaeration, minimization of photobleaching, inner filter effect, background corrections, and sorptive losses to system interfaces are described in refs *33* and *35*.

Biodegradation Experiment. We performed a biodegradation experiment of individual LABs using waters from MB. The procedure is fully detailed in Long (6). Seawater was collected in a 20-L glass carboy off Nahant, MA, a peninsula reaching out in the middle of MB (Figure 1), during rising tide in June, 1995. The water was transferred within 1−2 h in aliquots to 16 pre-cleaned 1-L glass volumetric flasks. Immediately before filling with seawater, the walls of each flask were plated with 100 μL of methylene chloride seeding solution containing the Alkylate 225 LAB mixture (ca. 33 ng total LABs/μL). A small amount of PCB congener #143 (1.8 ng/μL in 100 μL of isooctane; 99+% pure, Accustandard, New Haven, CT) was also added as a control for HOC biodegradation as PCBs are known to be environmentally recalcitrant relative to LABs. Three flasks were used as controls for LAB biodegradation by poisoning with 10 mg of mercuric chloride ($HgCl_2$) and 325 mg of sodium azide (NaN_3) (both from Fluka Chemie, Switzerland). The tightly capped flasks were stored in the dark in an incubator at 12 °C, the ambient water temperature measured at the time of sample collection. At the temperature and salinity of this water, the air-equilibrated dissolved O_2 concentration would be around 300 μM while the DOC concentration was around 100 μM (Table 3). Hence, even in the highly unlikely situation that all this recalcitrant seawater DOC was degraded, the microcosms would not be expected to become anoxic. To follow the course of LAB biodegradation, flasks were periodically sacrificed at the following times: 0 days (2 flasks), 1 day (2 flasks), 3 days (2 flasks), 5 days (2 flasks), 7 days (2 flasks and one control flask), 14 days (2 flasks and 1 control flask), and 21 days (2 flasks and 1 control flask). A yield standard in 100 μL of methanol containing known amounts of 1-C_{10}, 1-C_{11}, and 1-C_{13} LABs were added to each flask to determine the extraction efficiency. Subsequently, the incubated waters were extracted three times with 5 mL of *n*-hexane and 5 min of intense shaking. The combined hexane extracts were dried with anhydrous sodium sulfate and its volume was reduced to about 1 mL prior to analysis. A Carlo Erba HRGC 4160 was equipped and operated under identical conditions as for seawater LAB quantification, but with a flame ionization detector (FID). Individual LAB concentrations were corrected for the recovery of the internal standards.

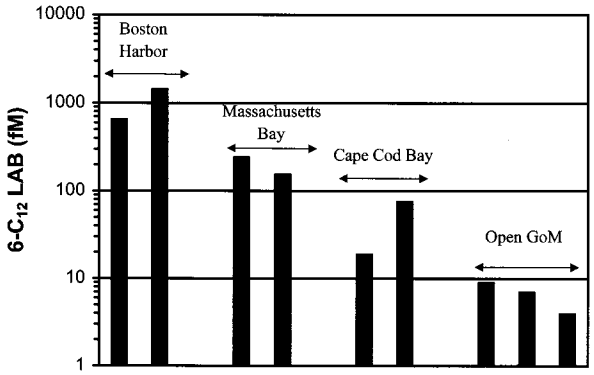

FIGURE 2. Particulate surface water concentrations of the 6-C_{12} LAB isomer in different regimes of the southwestern Gulf of Maine in July 1996.

Results and Discussion

LAB Inputs. LAB inputs via wastewater discharge into BH overshadowed all other LAB sources to the Gulf of Maine. In the year of our water sampling campaign (1996), this LAB loading to Boston Harbor was 2700 kg/year (*23*). We previously estimated the LAB input to the rest of the GoM from municipalities along its entire northeastern US and Canadian coastline from Halifax, Nova Scotia to Portsmouth, New Hampshire to be 3000 kg/year (*6*). Thus, we expect the BH input overwhelmed all other releases to the southwestern GoM. The monthly BH input data showed a weak seasonal cycle as effluent flows and LAB concentrations varied during the year, so the inputs in July were about 10% less than the annual average release rate.

Distribution of Particulate LABs in GOM Surface Waters. Given the trace concentrations of LABs in seawater and the risk of detergent contamination of the samples, it behooved us to consider the blank issue carefully. In addition to our use of non-LAS detergents and the shipboard "trace-HOC clean" techniques, we flushed our precleaned stainless steel sampling systems for several hours with ambient seawater before filtering over 1000 L at the offshore stations. Multiple-filter method blanks of individual LABs indicated a signal-to-noise ratio around 100 for BH samples and 5−40 in CCB and coastal GoM samples. Whenever the S/N was <3, the listed values in Table 2 are preceded by the "<" sign (e.g., open GoM 4) and in such cases a reliable I/E ratio could not be calculated.

Concentrations of individual LABs collected by filtration were observed to decrease in offshore transects from both Boston and Portland Harbors (Table 2). This is consistent with municipal wastewater being the dominant entry route of the LABs. Taking the concentration pattern of 6-C_{12} LAB as an example, its particle-associated surface water abundance was near 1 pM in BH, decreased to about 200 fM in MB and about 50 fM in CCB, and was on the order of 10 fM at the offshore GoM locations (Figure 2). The spatial distributions were also consistent with perception that waterborne transport followed a path through BH to MB and then CCB as expected from physical oceanography observations (*19*).

Unfortunately, there are no data available on individual LAB isomer abundances in ocean waters with which to compare. Eganhouse and Sherblom (*7*) reported 300−400 ng/L ΣLABs for an interior BH area collected in 1988 before the new primary sewage treatment facilities began operations. Assuming that 6-C_{12} was 7% of the ΣLABs (*24*), their BH data corresponds to around 100 pM 6-C_{12}. This higher concentration relative to our BH1 and BH2 was likely due to either their sampling much closer to a large combined sewer overflow than we did and/or to greater LAB discharges in the

TABLE 2. Concentrations of Particulate LABs in Surface Waters (pM) and Surficial Sediments (pmol/gdw) in the Gulf of Maine

	6-C_{12}	5-C_{12}	4-C_{12}	3-C_{12}	2-C_{12}	I/E ratio	5-C_{10}	5-C_{11}	5-C_{13}
Water Samples									
BH 1	0.66	0.60	0.47	0.39	0.71	0.80	0.39	0.76	0.26
BH 2	1.44	1.39	1.08	0.98	1.77	0.74	0.77	1.68	0.63
MB 1	0.24	0.18	0.085	0.024	0.020	3.3	0.058	0.11	0.088
MB 2	0.15	0.18	0.078	0.028	<0.011	2.9	0.062	0.091	0.11
CCB 1	0.019	0.019	0.015	0.005	0.014	1.1	0.011	0.007	0.015
CCB 2	0.076	0.074	0.059	0.049	0.10	0.72	0.016	0.050	0.062
PH	0.18	0.13	0.095	0.066	0.12	1.2	0.093	0.21	0.077
coastal GoM 1	0.034	0.031	0.022	0.021	0.072	0.57	0.008	0.016	0.017
coastal GoM 2	0.038	0.037	0.032	0.035	0.069	0.55	0.012	0.018	0.083
open GoM 3	0.009	<0.018	<0.009	0.007	0.014	0.3−1.3	0.004	<0.014	<0.012
open GoM 4	<0.014	<0.021	<0.010	<0.011	<0.023	n/c[c]	<0.009	<0.016	<0.010
GSWCH	0.004	0.009	0.003	<0.006	0.007	0.8−1.3	0.004	0.006	<0.008
Sediment Samples[a]									
MB 2	30	25	23	24	92	0.39	2.0	9.3	23
CCB 2	15	12	13	14	55	0.32	2.0	2.8	7.0
Portland Harbor	77[b]	77[b]	40	15	41	1.6	n/a[d]	70[b]	n/a[d]
coastal GoM 1	2.4[b]	2.4[b]	2.4	2.4	3.2	0.60	n/a[d]	2.8[b]	n/a[d]
open GoM 4	4.5[b]	4.5[b]	4.9	3.7	6.9	0.58	n/a[d]	2.8[b]	n/a[d]

[a] For all sediments, data from the 2−3 cm interval are reported. [b] For these sediments, the sum of the 6-C_{12} and 5-C_{12} LAB isomers were quantified. Data shown for each isomer are given as half total measured. [c] Not calculated since some compounds in ratio were not detectable. [d] These isomers were not analyzed in these samples.

TABLE 3. Surface Water and Surface Sediment Characteristics for Boston Harbor and Adjacent Waters in the Gulf of Maine during Stratified Conditions

	BH	MB	CCB
surface area (m^2)[a]	3.3×10^8	3.2×10^9	1.6×10^9
mixed layer depth (m)[b]	10	10	10
hydraulic residence time (days)[c]	5	30	45
POC (μM)	38	14	6.5
DOC (μM)	95	100	79
wind speed, u_{10} (m/s)[d]	5	5	5
porosity of surface sediments[e]	0.78	0.73	0.54
sedimentation rate (mm/year)[e]	4.6	3.1	3.7

[a] From (refs 53−56). [b] Assumed equal to mean depth in BH (*53*). Others derived from inspection of the ship's CTD data (Supplemental Information), consistent with typical summertime values summarized in ref *19*. [c] For BH from ref 21 and 53, average of range reported for MB and CCB (*19*). [d] Based upon daily observations at Logan Airport Boston and Portland, ME airport (*57*). [e] From Gustafsson and Gschwend (*27*).

TABLE 4. Characteristic Removal Rate Coefficients for 6-C_{12} LAB in Three Sub-Regions of the Gulf of Maine

process and parameter in eq 1	Boston Harbor	MA Bay	Cape Cod Bay
flushing, k_w ($year^{-1}$)[a]	36	12	8
vertical scavenging, k_s ($year^{-1}$)[b]	59	33	60
volatilization, $k_g = v_{tot}/z_{mix}$ ($year^{-1}$)[c]	27	27	27
photodegradation, k_{hv} ($year^{-1}$)[d]	<1	<1	<1
biodegradation, k_{bio} ($year^{-1}$)[e]	150	150	150

[a] From refs *53*−*56*. [b] From ^{238}U-^{234}Th disequilibria observed in this study. [c] Water−air transfer velocities calculated for $u_{10} = 5$ m/s, using molecular diffusivities approximated from 6-C_{12}-LAB molecular weight, and $\alpha = 0.67$ and $\beta = 0.5$ to estimate piston velocities, v_{tot} (*45*). [d] For indirect photolysis considering prospective reactions with $^1O_2$, ROO•, and HO•. [e] Using empirical rate observed in this study at 12 °C and with negligible degradation in the control. Note that the observed k_{bio} is likely to represent $f_w k_{d,bio}$.

past. Using the same assumptions, we also estimate particulate surface water concentrations for this LAB isomer at a deep-water dump site (DWDS 106) to have been of 70 pM (*14*). Still lower concentrations are calculated for coastal waters off San Diego (10 fM; ref 36) and in the Rhone Estuary (1−10 fM; ref 16). Hence, it appears that individual LABs occur in the picomolar range near waste inputs and decline to femtomolar levels in nearby waters.

Using our pairs of observations for each of the water bodies, the surface mixed layer water column (from areas and mixed layer depths; Table 3) inventories of the 6-C_{12} LAB isomer were about 1 kg in BH in July 1996 and 3 kg in the whole BH−MB−CCB system at that time. Given the reported wastewater discharge at that time (200 kg 6-C_{12}/year; again assuming that this isomer is 7.4% of the total LAB, ref 24), this corresponds to a turnover time in BH of only 2 days. Moreover, in this whole coastal system the ratio of the 6-C_{12} LAB inventory to its input rate implies a characteristic time of 5−6 days. Since this is significantly shorter than the corresponding hydraulic residence times (Table 3), processes besides flushing must account for much of the removal of this anthropogenic hydrocarbon.

Three-Phase Speciation of LABs. To evaluate the ability of different LABs to participate in various processes (eq 1), we estimated their distribution coefficients between water and (a) large particles and (b) colloidal particles. Organic-carbon normalized partitioning with large particles (K_{POC}) was estimated using linear regression with *n*-octanol−water partition coefficients, K_{ow} (Table 1). Appropriate values for partitioning to colloids present in the surface ocean are largely unknown. In the absence of any data for HOCs such as LABs, in this study we established colloid binding coefficients using the similarly hydrophobic compound, 1-methylperylene. In these fluorescence-quenching studies, we obtained the same fluorescence lifetime for the dominant component of 1-methylperylene's fluorescence in artificial seawater (fully dissolved; $\tau = 3.85 \pm 0.23$ ns) and in the quenched seawater system (partially colloid-associated; $\tau = 3.86 \pm 0.42$ ns). This is strong evidence for a static quenching mechanism, simplifying the derivation of binding coefficients using fluorescence quenching (e.g., *37* and *38*). Our time-resolved fluorescence quenching study of HOC sorption to suspended seawater colloids, when corrected for fluorophore losses due to simultaneous partitioning to the air−water interface (*35*), gave a D+C OC-normalized log partition coefficient (log $K_{D+C\ OC}$) for 1-methylperylene of 5.3. This is much lower than the log K_{oc} of 6.6 that may be estimated for this compound from K_{ow} regressions (*39*). Some of this difference is due to attributing colloid

sorption to the entire D+C OC pool; if only one-third of that pool acts as a colloidal sorbent, then the corresponding log K_{COC} for methyl perylene would be 5.8.

Available results from coastal colloid binding studies consistently reveal a lower affinity of HOCs to these submicron sorbents (reviewed in ref *40*). This difference has a significant impact on predictions of colloid-water partitioning in coastal waters. The smaller size (e.g., >90% <10 kD; e.g., ref *41*) and more polar composition of the carbohydrate-rich (*42*) seawater colloids, relative to soil and sedimentary geosorbents for which such regressions were developed, likely explains why actual colloid−water HOC partition coefficients are lower. In this paper, we estimated the three-phase speciation of LABs in surface seawater (Table 1) using the relationship: $\log K_{D+C\ OC} = 0.80 \log K_{oc}$ (*33*) and $\log K_{POC} = 1.00 \log K_{ow} - 0.21$ (*39*) with K_{ow} values from ref *43*.

With knowledge of these POC−water and (D+C OC)−water partition coefficients, the fraction (f) of any given LAB associated with each of these three "phases" was estimated (Table 1). Assuming equilibrium applied, most (60−90%) of each LAB should be associated with the POC fraction actually sampled in these coastal waters. Our calculations suggested that the dissolved and colloidal species were of lesser importance. The colloidal fraction was predicted to range from 0.06 to 0.07 in Boston Harbor to 0.22−0.23 in Cape Cod Bay for the C_{12} LABs.

Horizontal and Vertical Transport. On the basis of published hydraulic residence times, the rates of water-borne, horizontal transport out of each region become slower with successive transport from BH to MB and finally into CCB (Table 4). This, of course, implies diminishing fluxes due to water-borne transport from area to area.

On the basis of the disequilibrium between ^{238}U and ^{234}Th, the rates of particle-mediated LAB export to below the mixed surface layer, k_s values, only varied by a factor of 2 in the regions studied. We saw somewhat higher values in BH and CCB, the two shallowest regions and regions closest to the coast (Table 4). These k_s values of 30−60 $year^{-1}$ were of similar magnitude as previously reported for the Gulf of Maine (*30*, *44*). As a check on the ^{234}Th-derived LAB scavenging fluxes out of the water column mixed layer, we compared these to LAB accumulation fluxes calculated for the corresponding sediments dated using $^{210}Pb_{xs}$ (Table 3) and analyzed for their LAB content (Table 2). The fluxes (in nmol m^{-2} $year^{-1}$) of 6-C_{12}-LAB into sediments versus out of the surface water at two stations each in MB, CCB, and open GoM were 6 vs 6 and <9, 62 vs 51 and 80, and 37 vs 11 and 46. This close agreement is consistent with previous findings for similarly hydrophobic highly chlorinated biphenyls in the GoM (*30*), which lends further credence to the ^{234}Th-derived scavenging rates used here. These rates imply that scavenging by settling particles and transport to the sediments was a more important removal process than flushing.

Volatilization. Since no air measurements of LABs have ever been presented, we have assumed an atmospheric LAB concentration of zero and unidirectional sea-to-air transport to estimate a maximum volatilization sink flux. A rate of removal due to volatilization from the bulk mixed layer water (k_g) was estimated using a stagnant two-film model of gas exchange (*45*) acting on the dissolved (f_w) fraction (Table 1). Combining these estimates of f_w and k_g, we suggest that exchange into overlying air was of lesser importance than flushing and settling (Table 4).

Photodegradation. LABs do not undergo direct photolysis in aqueous solutions exposed to sunlight (*11*). As indirect or sensitized photolysis largely occurs through the action of photooxidants such as $^1O_2$, HO•, and ROO•, we attempted to estimate the reaction rates of specific LABs with these excited oxygen species. Since there are no data for either LABs specifically, nor for the concentration of the reactants in the Gulf of Maine, we used available rate data for compounds with similar structure and oxidant data for similar environmental regimes. A maximal (assuming oxidants present throughout the mixed layer) pseudo first-order rate coefficient was estimated as:

$$k_{h\nu} \le (f_w)\,(k_{1O2}[^1O_2] + k_{ROO}[ROO\bullet] + k_{OH}[\bullet OH]) = (0.04)\,(500\ M^{-1}\,s^{-1}\,[2 \times 10^{-14}\ M] + 0.18\ M^{-1}\,s^{-1}[10^{-9}\ M] + 3 \times 10^{9}\ M^{-1}\,s^{-1}[10^{-17}\ M])\,(3.2 \times 10^{7}\ s\ year^{-1}) = 0.04\ year^{-1} \quad (3)$$

where (f_w) is given in Table 2, k_{1O2} is for ethyl benzene (*46*), [$^1O_2$] was reported for seawater collected off Long Island (*47*), k_{ROO} is for a tertiary benzyl carbon (*48*), [ROO•] is from Mill et al. (*49*) for freshwater high in chromophores, k_{OH} is for cumene (*49*), and seawater [•OH] is from Mopper and Zhou (*50*). These estimates suggested that sensitized photolysis, acting on the fully dissolved species, was an insignificant loss process for LABs in coastal waters (Table 4).

Biodegradation. LAB biodegradation rates have not previously been determined in coastal seawater. There was negligible degradation in the biodegradation control samples. From our experiment (Figure 3), we deduced first-order removal rates of individual LAB isomers (e.g., the product, $f_w k_{r,d} = k_{bio}$, for 6-C_{12} in Table 4). In contrast to all the other process rate constants in Table 4, the value of k_{bio} was unique to each C_{12} LAB isomer, ranging from 150 day^{-1} for the internal isomer 6-C_{12} LAB to 680 day^{-1} for the more easily degraded external isomer 2-C_{12} LAB. Several previous investigators have reported selective biodegradation of the more external isomers (e.g., refs *10*, *11*, *13*, and *51*). This systematic variation in rate coefficients also implied that the I/E ratio, typically interpreted as an indicator of the degree of biodegradation (*8*, *14*), increased during the experiment as a result of more rapid degradation of the external isomers (Figure 3, and ref 6). Our empirical rates were determined in 12 °C MB water. The absolute rates are dependent on temperature, and thus could be somewhat higher during our field study, but we note that the field samples had temperatures around 12 to 16 °C (CTD data files available as Supplemental Information).

The I/E ratios seen in our field samples exhibited a complex pattern. Near the sources in Boston and Portland Harbors, the I/E was close to 0.8 as typical of industrial LAB mixtures. Consistent with near-source biodegradation, this ratio increased to about 3 in the water column of MB (Table 2). This was consistent with trends reported for other near-source regions such as Tokyo Bay (e.g., ref 13). Surprisingly, further away from the wastewater inputs (and presumably after more time for biodegradation), the I/E ratio became substantially lower. In surface water particles of CCB and GoM Proper, this ratio was in the range 0.5−1.2. We stress that I/E ratios were only considered for samples in which LAB concentrations were >3 times the blanks. Low values were also found in nonharbor surface sediments throughout the Gulf of Maine (Table 2). Several ratios were even lower than in the input material.

Three types of scenarios may explain these I/E trends. First, it may be hypothesized that there are additional LAB sources along the shoreline south of Boston or even at offshore sites (e.g., ship discharges). Alternatively, some unexamined removal process may have been active and enriching the external isomers. For example, if LABs, enriched in the internal isomers, substantially partitioned to the air−water interface or onto injected bubbles, water-to-atmosphere transfers of such interface-sorbed species might enhance water-to-air exchanges and cause the observed fractionation. Finally, it may be plausible that specific LAB congeners interconvert via a mechanism involving phenyl

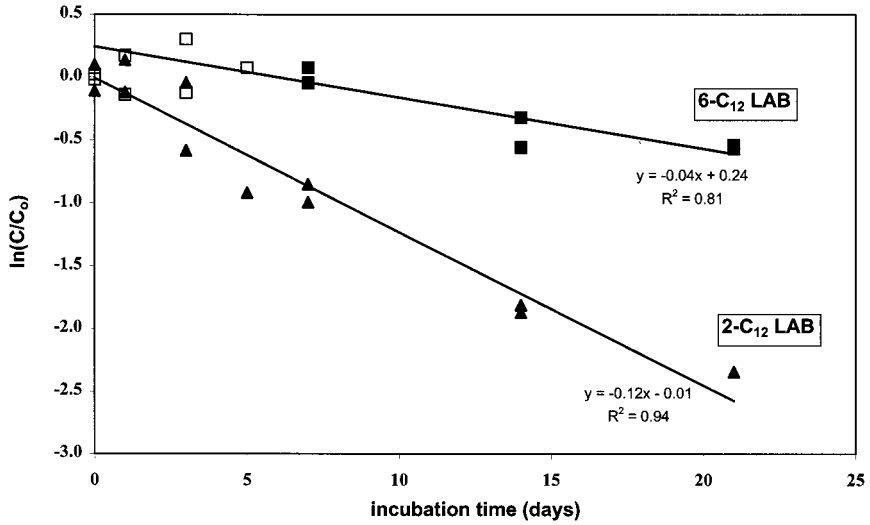

FIGURE 3. Log-transformed concentrations vs time allowing derivation of biodegradation kinetics of internal isomer 6-C_{12} LAB and external isomer 2-C_{12} LAB in 12 °C coastal seawater. Increasing lag periods (open symbols) were noted with internal alkyl-chain substitution (*6*) and degradation kinetics were derived from data following the lag period. Note the absence of initial lag and more rapid degradation for the external isomer.

group migration after an H-abstraction from the alkyl chain, with subsequent reacquisition of a hydrogen from the ambient natural organic matter. 1,2- and 1,4-shifts of phenyl on such substituted alkyl radical can occur (*52*). A random redistribution of the phenyl group on the C_{12}-alkane chain would yield I/E of 0.67, close to the values we observed in samples away from immediate source regions (Table 2). Such abstractions might be facilitated if LABs were enriched at the atmosphere−sea interface where exposure to atmospheric free radicals would be enhanced and enrichment of organic matter is known to occur. For now, simply interpreting I/E ratios as indicative of the extent of biodegradation at offshore locations appears questionable.

We sought further insight by assessing the distribution of 5-phenylalkanes with different chain lengths (Table 2). Unfortunately, the ratio, (5-C_{13} + 5-C_{12})/(5-C_{11} + 5-C_{10}), is highly variable between different industrial mixtures (personal communication, R. Eganhouse, United States Geological Survey, Reston, VA, October 2000). However, we found that the ratio of (5-C_{13} + 5-C_{12})/(5-C_{11} + 5-C_{10}) increased from 0.69 to 0.82 in the three BH and Portland Harbor locations to values between 1.6 and 4.0 for stations further away from the coast (calculated from data in Table 2). Vertical scavenging should lower the ratio as the more hydrophobic and sorptive congeners are more extensively particle-associated. If biodegradation is directly related to the fraction of each compound in the dissolved phase (i.e., f_w), then this process would cause the ratios to increase. Thus, we suspect the 5-phenylalkane fractionation we see was indicating the increasing importance of biodegradation relative to sedimentation in offshore waters.

Comparison of Field Measurements with Simulations. To help distinguish between the various hypotheses offered to explain the observed LAB fractionations, we performed mass balance box modeling of individual LABs through the BH−MB−CCB system (boundaries delineated in Figure 1 and sizes given in Table 3). We solved for the steady-state concentrations ($C_{t,ss}$) expected from eq 1 using:

$$C_{t,ss} = (I_t/V)/(k_w + f_w k_g + f_w k_{bio,d} + f_w k_{photo,d} + f_p k_s) \quad (4)$$

in which we assumed that both input from the atmosphere and reactions of sorbed species were negligible processes. We used source functions, phase speciation and process rates discussed above. We emphasize that we did not do this modeling to "fit" our empirical data, but rather to identify gaps in our current understanding of the sources and sinks affecting such hydrophobic contaminants. We also tested the sensitivity of the model by systematically varying one term of the model at a time. The individual terms were varied as follows: k_w (± factor of 1.2), k_s (± factor of 2), k_{bio} (± factor of 5), K_{POC} (± factor of 1.5), and $K_{D + C\ OC}$ (± factor of 3). Furthermore, the model was run both with and without considering colloids (i.e., two-phase speciation). The output of these calculations was used to put "bounds" on the model predictions (shown in Figure 4).

The modeled results for the 6-C_{12} and 2-C_{12} LAB isomers match our observations to within about a factor of 2 within Boston Harbor (Figure 4). The model calculation also yielded a reasonable match to the observed I/E ratio (predicted 0.9 and observed 0.8). As the LABs were mixed out into MB amended with 360 kg LABs/year from the South Essex discharge (*6*), the modeled 6-C_{12} LAB concentrations were again in good agreement with what we observed for this isomer (Figure 4a). However, the 2-C_{12} LAB and 3-C_{12} LAB congeners, the two congeners most likely to be lost via biodegradation, were about 10 times lower in concentration in MB than predicted by the model (Figure 4b for 2-C_{12} LAB). Given these observations, it is reasonable to suggest that we underestimated biodegradation in this region. A 5-fold increase of k_{bio} yielded a prediction of I/E in MB of 2.0 to be compared with the observations of 3.1. Allowing this range of k_{bio} also brings the predicted concentration range within a factor of 3 of observations. Obviously, our limited biodegradation data, obtained with near-source organisms and using spiked LAB, may not have been suited to predicting biodegradation in far-field regimes with much lower ambient LAB concentrations.

The observed 6-C_{12} LAB concentrations in CCB were again similar to the predicted concentrations (Figure 4a). However, if we allow greater removal (e.g., by biodegradation) of 2-C_{12} LAB in MB, then an additional source of LABs into CCB would be needed for model predictions to match our observations. The observed I/E ratio of 0.8 in CCB may also imply a "fresh" source of LABs to this region.

On the basis of our modeling, several processes were expected to influence these LABs to similar extents. The independently parametrized apparent first-order process rates were multiplied by the mean concentrations observed in each regime. The inputs to MB and CCB "boxes" were

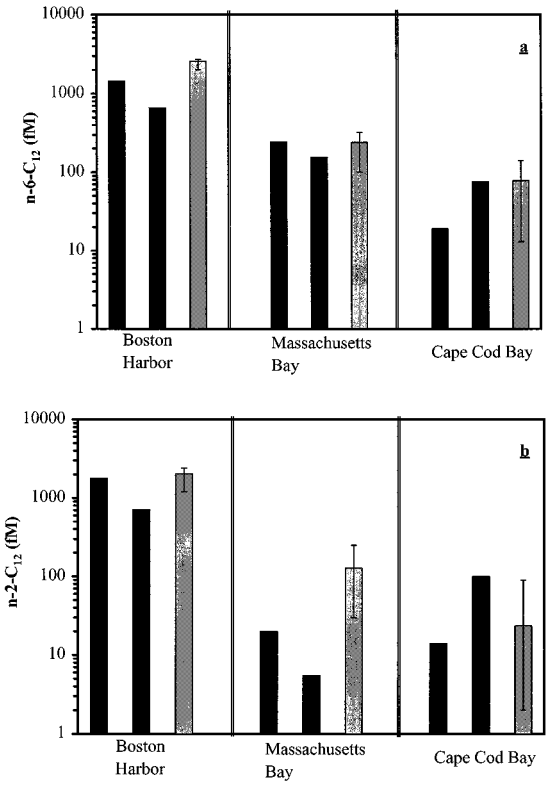

FIGURE 4. Comparison of observed (dark bars) and model predicted (grey bars) concentrations of 6-C_{12} LAB (a) and 2-C_{12} LAB (b) isomers in Boston Harbor, Massachusetts Bay and Cape Cod Bay surface waters in July 1996. Better agreement between the two sampled locations in each regime and between model and observations were noted for the internal isomer, 6-C_{12} LAB. Away from the immediate source region, this harbor-released pollutant is accurately predicted within a factor of 2. A larger uncertainty is found in the simulations of the 2-C_{12} LAB isomer more susceptible to biodegradation. The vertical scale bar on the model predicted concentrations denote the sensitivity range of the prediction resulting from varying the value of k_{bio} by a factor of 5 in either direction.

taken as the flushed output from the respective upstream box. In each of the BH, MB, and CCB surface water "boxes", horizontal flushing, vertical scavenging, and microbial degradation were all significant removal mechanisms (Figure 5). The sinks due to indirect photolysis and volatilization were unimportant in the overall mass balances. Because of increased residence time in the far field boxes, scavenging and biodegradation were predicted to become increasingly significant relative to flushing as the LAB-containing water parcel ages. As indicated by the 5-phenylalkanes, biodegradation is predicted to be an increasingly important LAB sink.

At the end of their transit, only about 1% of the LABs released in Boston Harbor was calculated to be exported beyond Cape Cod Bay (Figure 5). Since the data-modeling mismatch becomes most pronounced for isomers of higher biodegradability, the more persistent 6-C_{12} LAB isomer is the preferred LAB tracer of HOC wastewater input (see also ref *17*).

Running the model calculations with and without consideration of colloidal species did not have a large affect on the calculated outcomes. Without colloidal associations, we would have expected the same flushing, the same vertical transport, increased volatilization (factor of 2−3), and the same biodegradation (because our empirical approach determined the product, $f_w k_{bio,d}$). Since volatilization appears insignificant in this case, one would have arrived at very similar modeling predictions. Thus even though the LABs are very hydrophobic, colloids would have only a very small impact on LAB cycling since this fraction is estimated to be so small in these coastal seawaters.

To summarize, we believe wastewater inputs, flushing, and vertical scavenging of LABs were probably reasonably constrained. The in situ rates of microbial reactions certainly require future investigation. For HOCs that are less susceptible to biodegradation such as internal LAB isomers, it appears that we are at present able to predict the coastal fate of the wastewater-introduced HOCs within a factor 2. But given the unusually low I/E ratios in offshore seawater and sediment, we believe that some process substantially affecting LABs is not accurately represented as yet.

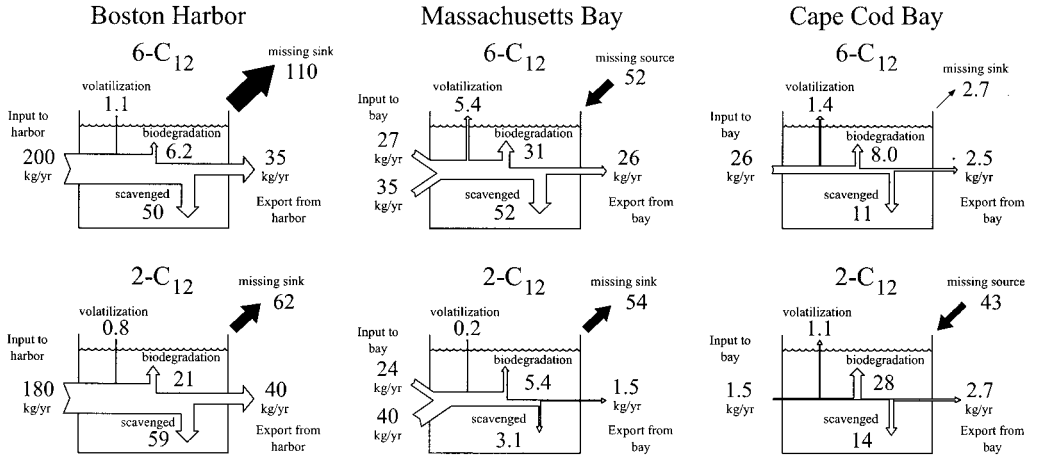

FIGURE 5. Modeling results illustrated for the 6-C_{12} and 2-C_{12} LAB isomers in the summertime surface waters of Boston Harbor, Massachusetts Bay and Cape Cod Bay. The independently parametrized apparent first-order process rates were multiplied by the mean concentrations observed in each regime. The inputs to MB and CCB "boxes" were taken as the flushed output from the respective upstream box. Note the additional wastewater input to MB from South Essex primary treatment plant (*6*). The two isomers do not have identical environmental fates. The simulation indicates that sedimentation is the dominant sink process for 6-C_{12} LAB while biodegradation may be more important for the 2-C_{12} LAB isomer. Comparison of the simulated concentrations with our duplicate observations in each regime (Figure 2) suggests that there is a missing sink for both isomers in Boston Harbor of a similar magnitude as the accounted sinks. For the 6-C_{12} LAB isomer, there is apparently good accountability of the overall fate in MB and CCB, whereas a significant missing sink of the external isomer is noted in MB.

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Supporting Information Available

CTD data from lower Cape Cod Bay, upper Cape Cod Bay, Boston Harbor, inner Massachusetts Bay, outer Massachusetts Bay, Stellwagon Basin, Wilkinson Basin, Platt's Bank, and off Casco Bay. This material is available free of charge via the Internet at http://pubs.acs.org.

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