Xenobiotic Organic Compound Cycling In Coastal Waters

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LONG-TERM GOAL

Our long-term goal is to develop the basis for predicting the fates of xenobiotic organic chemicals in harbors and coastal marine environments. To this end, we seek to build a flexible modeling approach that is capable of yielding estimates of chemical concentrations in space and time, and which is tunable for various compounds and coastal environments of interest. Such predictions are necessary to allow us to manage wisely our coastal discharges and to evaluate the need to clean up existing conditions.

OBJECTIVES

In order to assess xenobiotic organic chemicals which are hydrophobic (HOCs) in coastal marine environments, we must be able to (1) characterize each chemical's speciation, and (2) evaluate the rates of processes affecting particles in coastal seawater. The first objective requires us to examine the distribution of contaminants like PCBs and PAHs among dissolved, colloidal, and settling-particle phases. Moreover, we seek to find properties of the sorbates, sorbents, and solutions from which these "phase" distributions can be estimated *a priori*. The second objective requires us to assess quantitatively the fluxes of solids from the water column to the sediment beds below.

APPROACH

In the last year, we have pursued two approaches for examining the cycling of organic contaminants in coastal seawaters. First, we used fluorescence observations of the probe fluorophore, methyl perylene, to observe the importance of partitioning of such hydrophobic organic chemicals to the air-seawater interface. Secondly, we sought to assess the effectiveness

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of our chemical fate modeling by contrasting our predictions of the concentrations of linear alkyl benzenes, a group of hydrophobic organic compounds with a well-defined source to coastal water, with measurements we have made of their occurrence in coastal seawater and sediments. In this effort, we applied our U238-Th234 derived sedimentation rate coefficients, along with particulate concentrations of the organic compounds, to calculate the export fluxes of those organic chemicals from the water column.

WORK COMPLETED

We used the fluorescent probe, 1-methylperylene, to measure the affinity of hydrophobic (as opposed to amphiphilic) compounds for the air-water interface (Gustafsson and Gschwend, in press). We completed this investigation by demonstrating that our findings fit an extrapolation of literature data available for much less hydrophobic substances.

We also used linear alkyl benzenes (LABs) as molecular markers of coastal pollution in large urban harbors to examine our ability to predict the fate of HOCs released in urban harbors to and within adjoining offshore waters. The approach was applied to Boston Harbor and the adjoining waters of Massachusetts Bay and Cape Cod Bay. Estimates were made of both the phase speciation and the rates of the different processes affecting each HOC's fate. These parameters were used to make predictions of LAB concentrations, and these predictions were compared to our field measurements.

RESULTS

We found the water-air/water interface partition coefficient for the polycyclic aromatic hydrocarbon, methylperylene, to be: $K_{w\text{-}awi} = 1.2\ \text{mol/cm}^2_{awi}/(\text{mol/mL}_w)$. This result is consistent with an extrapolation of partition coefficients reported in the literature for much less hydrophobic PAHs, distributing themselves between the same interface and air. In fact, our combined results lead to a predictive equation for water/air-water interface partition coefficients of aromatic hydrocarbons:

$$K_{w\text{-}awi} = 10^{-10.4} (P_L)^{-0.20} \gamma_w$$

where $K_{w\text{-}awi}$ is the partition coefficient in (mol per cm^2 of interface/ mol per mL of solution),
P_L is the (hypothetical) liquid vapor pressure in atmospheres, and
γ_w is the aqueous activity coefficient in reciprocal mole fraction.

Our results demonstrate significant partitioning from bulk water to the water/air interface for a hydrophobicity range relevant to many xenobiotic compounds (e.g., 5-ring PAHs, highly chlorinated PCBs).

The mass balance box modeling of LABs in Boston Harbor and the adjoining waters of Massachusetts Bay and Cape Cod Bays suggested that fates of LABs are controlled to similar extents by (1) horizontal flushing, (2) vertical scavenging, and (3) microbial degradation. In contrast, the sinks due to indirect photolysis and volatilization were initially suggested to be minimal. By comparing these modeling predictions with our field measurements of LABs in seawater, we found that we could not match those observations without adding an additional sink to the modeling calculations. Moreover, that sink must preferentially eliminate "internally substituted" LABs over their "externally substituted" isomers. In light of these discrepancies and our observations of the substantial partitioning of hydrophobic compounds to the air-water interface (Gustafsson and Gschwend, in press), we speculate that the "missing sink" may involve (1) partitioning of LABs to the air-water interface and then either (2a) enhanced mass transfer to the atmosphere or (2b) enhanced transformations due to interactions with atmospheric oxidants.

IMPACT

We anticipate that the very substantial partitioning of hydrophobic compounds (note: these compounds must not be confused with amphiphiles) from aqueous solution to the air-water interface may have important ramifications for the intensities of numerous environmental processes affecting fates of those compounds. For example, water-to-air transfers could be greatly enhanced over current model predictions which identify the water-side diffusive boundary layer as the critical bottleneck for export of PAHs to the atmosphere. Likewise, transformations of such substances in coastal seawater environments may include, not only solution phase processes, but also reactions with tropospheric species (e.g., hydroxyl radical) since these low-solubility organic pollutants may occur at important concentrations adjacent to marine air.

TRANSITIONS

Our work will influence efforts to establish the capacities of harbors and coastal environments to act as receiving waters for hydrophobic organic pollutants (such criteria are needed by the Navy to evaluate their discharge practices at their harbor facilities.) Our findings will also assist colleagues trying to promote the biodegradation of hydrophobic pollutants, a process that is undoubtedly controlled by those chemicals' bioavailabilities.

RELATED PROJECTS

All of the Navy-supported projects examining the biodegradability of hydrocarbons are related to our work in that the speciation of those hydrocarbons plays a central role in controlling microbial access to those prospective hydrocarbon substrates.

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