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Fate of Benzene in a Stratified Lake Receiving Contaminated Groundwater Discharges from a Superfund Site

LUKAS Y. WICK,[†] KRISTOPHER MCNEILL,[‡] MICHAEL ROJO, EDI MEDILANSKI,[†] AND PHILIP M. GSCHWEND*

Ralph M. Parsons Laboratory, 48-415, Department of Civil and Environmental Engineering, 15 Vassar Street, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Predicting the fate of benzene in aquatic environments, and estimating corresponding human exposures, is critically dependent on knowledge of this carcinogen's biodegradation rate under the site-specific conditions. We used three approaches for quantifying this key fate process: (1) short-term (hours) observations of benzene loss in laboratory incubations of representative water samples, (2) whole-lake benzene mass balance studies, and (3) modeling of the temporal evolution of benzene vertical profiles in the lake. Our field site, the Halls Brook Holding Area (HBHA), continuously receives benzene input (about 20 μM or 1.5 ppm) into its anoxic hypolimnion via discharge of saline groundwater from an adjacent Superfund site (Industri-Plex in Eastern Massachusetts.) Using summertime, lake water samples in the laboratory, we found benzene was degraded in three metalimnion samples at rates between 1 and 2.5 d^{-1}. An epilimnion sample yielded a similar result, but no degradation was observed in another epilimnion sample. Losses were $\leq$0.04 d^{-1} in a sulfate-rich hypolimnion sample. Since benzene loss could be inhibited by filtration or with a mixture of poisons and antibiotics, it was apparently being biodegraded. In the whole-lake mass balance studies of benzene, it was found that approximately 80% of the benzene entering the lake was degraded during the water's residence in the lake. Vertical distributions of benzene in the HBHA water column indicated that the chief sink of benzene was located in the metalimnion. A two-month progression of summertime profiles of benzene concentration vs depth was fitted well using a dynamic model, CHEMSEE, and assuming that the only sinks were epilimnetic flushing, water-to-air exchange, and biodegradation in a 0.4 m-thick metalimnetic layer at 2 d^{-1}. The biodegradation rate derived from such whole-system study appears more dependable than rates deduced from grab samples, and we suggest that we must learn to predict these intact-system rates.

Introduction

Benzene is a common environmental contaminant. It has been widely used as a solvent and an industrial intermediate. It is also a common component of coal tars and fuels such as gasoline. The bone marrow toxicity and carcinogenic potential of benzene for both humans and animals (*1*, *2*) have inspired frequent study into this aromatic compound's persistence in the environment (*3*, *4*).

Accurately assessing the environmental fate of benzene is hampered by the difficulty in predicting this chemical's biodegradation rate in situations of interest. The oxic biodegradation of benzene is well-established both in the laboratory and in field studies (e.g., in aquifers (*5*−*7*), landfill leachates (*8*), and surface waters (*9*)). Laboratory experiments have found pseudo-first-order degradation rates ranging from zero to 18 d^{-1}. Likewise, field observations indicate a wide range of rates; for example, Wakeham et al. (*9*) observed no biodegradation of benzene in the MERL mesocosms in the winter and rates of about 0.2 d^{-1} in the summer. When molecular oxygen is absent, benzene is still biodegraded if nitrate is present (e.g., refs *10* and *11*). However, in the absence of O_2 and NO_3^-, biodegradation of benzene is not certain. At many anoxic field sites, no benzene degradation has been seen (e.g., refs *12*−*14*), while at other sites, the investigators report detecting this biological process (e.g., ref *15*). Recent *laboratory* studies indicate that certain iron- or sulfate-reducing microorganisms can degrade benzene (e.g., refs *16*−*23*; for review, see ref *24*). Thus, it is unclear why benzene is persistent in many anoxic field sites, since ferric iron and sulfate are widespread environmentally. Moreover, it remains impossible to estimate a priori what the biodegradation rate will be in any particular case of interest. Some workers feel that reliable degradation rate constants can only be determined in situ (*25*, *26*).

Here we present a study of benzene cycling in a small lake, the Halls Brook Holding Area (HBHA). The HBHA receives benzene-contaminated groundwater input from an adjacent Superfund site (Industri-Plex). On Industri-Plex, large amounts of crude benzene (approximately 8000−21000 metric tons (*27*)) were converted to phenol during World War I. The groundwater just north of the lake contains a large benzene plume with peak concentrations near 60 μM (ca. 5 ppm) (*28*). The origin of the plume is near the area of former distillation and storage facilities of crude benzene during World War I (*28*, *29*). We have previously reported that this benzene is presently discharging to the HBHA at about 30 kg/year (*27*). The lake is stratified year round with bottom waters always anoxic and sulfate-rich, while the epilimnetic waters are always oxic. The steady input of benzene into HBHA provided a unique opportunity to assess the importance of degradation in both oxic and anoxic environments.

In addition, the HBHA may also play an important role in controlling the delivery of benzene and other toxic substances to downstream receptors. In light of the reported childhood leukemia cluster seen in East Woburn in the decade from 1969 to 1979 (*30*), understanding the potential for downstream transport of this putative leukemogen is of particular interest.

Accordingly, our purposes were 3-fold: (1) to delineate the cycling of benzene in this aquatic environment with a particular emphasis on ascertaining whether biodegradation was occurring in the oxic and anoxic parts of the lake, (2) to assess our ability to obtain estimates of in situ benzene degradation rates, and (3) to characterize the role the HBHA

* Corresponding author phone: (617)253-1638; fax: (617)253-7395; e-mail: pmgschwe@mit.edu.

[†] Present address: Swiss Federal Institute of Technology, IATE/P, CH-1015 Lausanne, Switzerland.

[‡] Present address: Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455.

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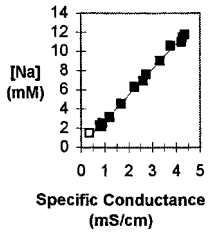

FIGURE 1. Water column sodium ion concentrations (mM) for samples collected on 8/14/98 vs conductance (mS/cm) measured in the field with a portable conductance probe. Filled symbols are from station A ($n = 16$, $0.798 < \kappa < 4.355$ mS/cm). The open symbol is from Halls Brook surface input ($\kappa = 0.353$ mS/cm). The solid line corresponds to a linear least-squares regression for all data and has $m = 2.66 \pm 0.04$ mM (mS/cm)$^{-1}$, $b = 0.15 \pm 0.10$ mM, and $r^2 = 0.997$.

may have played in controlling benzene exposure to downstream receptors.

Experimental Section

Description of Field Site. The HBHA is an artificial, shallow (≤4.8 m), 0.017-km^2, 40000 m^3 lake in the Aberjona Watershed in Woburn, MA (*31*). It is a meromictic lake, located immediately to the south of the Industri-Plex Superfund site. Groundwater from this former industrial area enters the northern end of the HBHA and carries high benzene and salt concentrations. The surface of the lake receives substantial inflow from Halls Brook and some seasonally ephemeral small drainages in the north (e.g., Atlantic Ave. Drainway) of insignificant water input during most of the period reported here. The lake's outflow joins the Aberjona River approximately 1 km downstream. The Aberjona continues south past the old water supply wells G and H (1.8 km from HBHA), before entering the Upper Mystic Lake.

Sampling and Analysis. At regular intervals from June 1997 until January 1998, benzene, temperature, conductance, and dissolved oxygen (DO) profiles were taken at a station at the southern end of the lake at its deepest point (Station A, depth: 4.8 m). Temperature, DO, and conductance were measured with a Hydrolab MiniSonde water quality multiprobe (Hydrolab Corp., Austin, TX). Streamflow rates were determined with a Marsh and McBirney model 201 portable water current meter, and discharges were calculated using current velocities and cross sectional areas. Water for benzene analyses was pumped with a portable Masterflex pump using Teflon tubing, collected in ground-glass stoppered, 60-mL biological oxidation demand (BOD) bottles with no headspace, kept isolated from the air in the dark at 4 °C, and analyzed within 7 days.

Before analysis, water samples were transferred to clean, airtight glass syringes (Popper & Sons, New Hyde Park, NY) for delivery to the Tekmar purge-and-trap system. For the analysis of benzene, 5-mL samples were concentrated for 5 min with a Tekmar LSC2000 purge-and-trap concentrator using a Tenax/silica gel/charcoal trap. A Carlo Erba HRGC 5160, equipped with a 75 m, 1-μm film thickness, DB5 capillary column (5% phenylmethylpolysiloxane, J&W Scientific, Folsom, CA) and a flame ionization detector, was used. 1,4-Bromofluorobenzene (BFB) was used as an internal standard. Benzene was identified by matching its GC retention time and mass spectrum (Hewlett and Packard 5995B GC-MS) with data obtained using an authentic standard (ChemService, West Chester, PA, purity: >99.5%).

On 8/14/97, the water column samples were also analyzed for Na by atomic emission spectroscopy on a Perkin-Elmer atomic absorption spectrometer. The Na concentrations were highly correlated with conductance measurements (Figure 1).

Air−Water Equilibration Experiments. To ascertain the water concentrations at equilibrium with air near the HBHA, 1-L jars containing water were exposed to the atmosphere between September 18−21, 1997 at the northern and southern ends of the HBHA. Surface water of the Upper Mystic Lake (Winchester, MA) was also sampled on September 14, 1997. In each case, the water was transferred at the site to clean, airtight, glass syringes and analyzed for benzene in the lab as described above.

Photochemistry Experiments. The potential for singlet oxygen ($^1O_2$) formation in HBHA surface water was examined as described in the literature (*32*). Briefly, furfuryl alcohol (Fluka) was added to surface water samples (Aug 21, 1996, DOC = 10 ppm) to give a final concentration of 2×10^{-5} M. These samples were irradiated under sunlight on the same day by placing them in 1.3 cm o.d. × 10 cm quartz tubes on a black, nonreflective background, inclined at about 30° from horizontal with the upper end pointing due north. Over time, samples were sacrificed and analyzed for furfuryl alcohol by reverse-phase HPLC (Hewlett-Packard 1050 Series HPLC; Alltech, Adsorbosphere C18 (5 μm) column) with acetonitrile: water (65:35) as the eluent. Detection was at 219 nm. A correction factor for the geometry of the photoreaction vessel of 2.2 was applied (*33*).

In Vitro Biodegradation Experiments. *Epilimnion*. Water was collected in 330-mL BOD bottles, 20 cm below the lake surface near the outflow of HBHA on Aug 7, 1997 (water temperature 24 °C) and again on Aug 12, 1997 (23 °C) and stored on ice in the dark. In the laboratory, the water was transferred to 50-mL airtight syringes and kept at the temperature observed in the lake. Due to low benzene concentrations, the water samples were spiked using benzene-saturated water to have between 15 and 17 nM (1.1 ppb) initial benzene. Negative controls were filtered through 0.2 μm pore-sized Millipore filters. All flasks were stored in the dark. Time zero was defined as the time when the control syringe was filtered. Aliquots were periodically removed and analyzed for benzene as described above.

Hypolimnion. On July 16, 1997, water (DO: <0.2 ppm, 12 °C) was pumped into 330-mL BOD bottles from the hypolimnion, 0.5 m above the sediment bed. The BOD bottles were allowed to overflow three times their volumes and then sealed airtight with no headspace; at the lab, water was transferred to 50-mL airtight glass syringes. The syringes were kept in the dark in a glovebox under nitrogen and periodically subsampled for benzene analysis.

Metalimnion. On Aug 1, 1997, a biodegradation experiment simulating the mixing in the metalimnion was performed. Water from 1.1 m depth (46 mL with DO: 0.35 ppm, 1513 μS/cm, 18.5 °C, benzene at 2.5 ppb or 32 nM) was combined with water from 1.3 m (4 mL with DO: 0.19 ppm, 2110 μS/cm, 18.5 °C, benzene at 100 ppb or 1.3 μM) in a 50-mL airtight syringe. This resulted in an initial benzene concentration of about 90 nM (17 ppb) with a DO of ca. 0.3 ppm. On Aug 14, 1997 (depth: 1.5 m, DO: 0.26 ppm, 1200 μS/cm, 19.5 °C) and on Sept 4, 1997 (depth: 1.6 m, DO: 5.2 ppm, 680 μS/cm, 17.5 °C), water was taken from the metalimnion and was used without amending. On those dates, we attempted to inhibit biodegradation in parallel samples by adding chloramphenicol (5 mg/L), tetracycline (5 mg/L), 37 μM $HgCl_2$ (10 mg/L), and 5 mM NaN_3 (325 mg/L).

Whole-Lake Mass Balance Calculations. Water- and salt-balance calculations were performed to establish the magnitudes of the important flows in the HBHA. The water balance was assumed to be at steady state and given by

$$d(H_2O)/dt = 0 = Q_{HB} + Q_{AAD} + Q_{GW} - Q_{out} \qquad (1)$$

where Q_{HB}, Q_{AAD}, Q_{GW}, and Q_{out} are the Halls Brook, Atlantic

Avenue Drainway, groundwater and outlet flows, respectively. Three of the four flow terms (Q_{HB}, Q_{AAD}, and Q_{out}) were measured directly, leaving Q_{GW} as the balance. It is important to note that we assumed the water balance was at steady-state. By contrast, the salt inventory of the lake was not constant, with salt tending to accumulate in the lake during low rainfall periods and being flushed out episodically (during rain storms).

In the salt balance calculation, field conductance measurements were used as a measure of the salt content of the water. For the calculation, the conductance values were converted into sodium (Na) ion concentrations using the correlation obtained on 8/14/97 (Figure 1). This was done because we knew that sodium was very closely correlated with conductance. The Na mass balance equation is

$$d(\mathrm{Na})/dt = I_{\mathrm{HB}} + I_{\mathrm{AAD}} + I_{\mathrm{GW}} - O - F \qquad (2)$$

where I_{HB}, I_{AAD}, and I_{GW} are the inputs of sodium from Halls Brook (HB), Atlantic Avenue Drainway (AAD), and groundwater, O is the Na lost through the outlet, and F is the Na removed by episodic flushing events. The I and O terms are the product of the flow and Na concentration measured during each field campaign (i.e., Q[Na]). The HB, AAD, and outlet contributions were determined by measuring the flows and conductances of these streams. The change in the salt-content, $d(\mathrm{Na})/dt$, was calculated from integration of the Station A vertical salt profiles

$$\frac{d[Na]}{dt} = \frac{[\int_0^{4.5}[Na]_z V_z dz]_{t_2} - [\int_0^{4.5}[Na]_z V_z dz]_{t_1}}{t_2 - t_1} \qquad (3)$$

where $[Na]_z$ is the concentration of sodium in each depth interval, V_z is the volume of water in the lake in each depth interval, and t_2 and t_1 are the times at which successive field measurements were made.

The magnitude of the episodic flushing term, F, was estimated by using our observation that the halocline typically deepens to about 2 m after major storms. Thus, we calculated the storm-derived Na losses using the salt profiles observed before each storm and assuming the upper 2 m of water became a 1.6 mM Na solution (600 μS/cm) after each rain event of >1 cm in 24 h:

$$\frac{d[Na]}{dt} = \frac{[\int_0^{2}[1.6]_z V_z dz]_{t_2} - [\int_0^{2}[Na]_z V_z dz]_{t_1}}{t_2 - t_1} \qquad (4)$$

There were 15 such events clustered unevenly over the observation period, resulting in greater flushing between certain sampling intervals than between others. Estimated in this way, episodic flushing removed an average 15 ± 5% of the total Na inventory per rain event.

The final term, I_{GW}, was determined as the balance of the other terms. However, from our temperature and conductivity surveys of the lake, we know this groundwater flow must be separated into low-conductance (350 μS/cm) and high-conductance (12,000 μS/cm) components. The high-conductance flow was the one of major interest since it was responsible for carrying the majority of the salt and all of the benzene into the HBHA. Thus it was necessary to separate the infiltrating groundwater into *high conductance* and *low conductance* components. To this end, we defined the salt and water balances for the groundwater as

$$Q_{GW}\kappa_{GW} = Q_{high}\kappa_{high} + Q_{low}\kappa_{low} \qquad (5)$$

$$Q_{GW} = Q_{high} + Q_{low} \qquad (6)$$

with κ_{high} as 12 mS cm^{-1} and κ_{low} as 350 μS cm^{-1}, the average

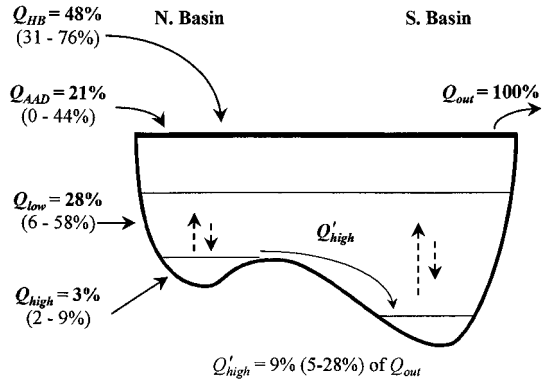

FIGURE 2. Schematic representation of the important components of the Halls Brook Holding Area water balance for the period June 1997 through January 1998.

value for the shallow groundwater conductance measured outside the benzene plume by other workers (*34*). The calculated values for Q_{high} and Q_{low} are available in the Supporting Information.

Because benzene was chiefly measured at the deepest point of the southern basin (Station A), and not in the northern basin where Q_{high} enters the lake, a derivative of Q_{high} denoted Q'_{high} was used. This flow is the diluted Q_{high} flow that fills the southern basin from the bottom (Figure 2.) This flow, Q'_{high}, was calculated by [(12 mS cm^{-1})/$\kappa_{hypolimnion}$] Q_{high} where $\kappa_{hypolimnion}$ is the value observed at the bottom of the water column at Station A.

In the second stage of the calculations, the flows established by the salt- and water-balances were used to estimate the magnitude of the benzene biodegradation in the HBHA. The mass balance was given by

$$d(\mathrm{C_6H_6})/dt = I - O - G - F - B \qquad (7)$$

where I is the input, O is the outlet loss, G is the gas exchange loss, F is the loss due to episodic flushing events, and B is biodegradation loss. The sole benzene source was assumed to be the high conductance groundwater, Q_{high}; however, since we only measured benzene in the hypolimnion at Station A, we used the product of Q'_{high} and the benzene concentration measured at Station A to set the input term (I). The outflow term (O) was set using the temporally varying flows and the measured concentrations of benzene in these flows. The water-to-air exchange (G) was calculated as the product of $(A)(v_w)[\mathrm{C_6H_6}]_{z=0}$, where A is the lake surface area, v_w is the water-to-atmosphere transfer velocity (0.5 m d^{-1}) (*35*), and $[\mathrm{C_6H_6}]_{z=0}$ was the surface water benzene concentration. The change in the benzene-content, $d(\mathrm{C_6H_6})/dt$, was calculated in the same manner as $d(\mathrm{Na})/dt$ (eq 3), from integration of the Station A vertical benzene profiles. The magnitude of the benzene loss due to episodic flushing events was estimated by replacing the upper 2 m of the water column with water that contained no benzene for each major rain event (>1 cm in 24 h):

$$\frac{d[\mathrm{C_6H_6}]}{dt} = \frac{-[\int_0^{2}[\mathrm{C_6H_6}]_z V_z dz]_{t_1}}{t_2 - t_1} \qquad (8)$$

This resulted in an average removal of 10 ± 5% of the total benzene inventory per rain event. The whole-lake biodegradation rate (B) was calculated as the difference between the input and other outputs, $B = I - O - G - F - d(\mathrm{C_6H_6})/dt$.

Computer Modeling of Vertical Profiles. Modeling was performed on a personal computer using CHEMSEE (*36*). We chose to model the ten-week period from 6/18/97 to

8/28/97 because several regularly spaced measurements of conductance and benzene vertical profiles had been obtained. Because the simulation end dates were chosen to coincide with sampling dates, the actual simulation times varied between 6 and 8 days. The depth of the lake (4.8 m), number of boxes (*45*), and vertical eddy mixing diffusivities for the epilimnion (5 $m^2\ d^{-1}$), metalimnion (0.01 $m^2\ d^{-1}$), and hypolimnion (0.03 $m^2\ d^{-1}$) were held constant for all of the simulations. The eddy mixing diffusivities were obtained from previous fitting of the HBHA conductivity profiles (*31*, *37*). The surface flows in and out of the lake were calculated from rainfall data using an empirical algorithm

$$Q_{HB} = Q_{base} + 0.5V_0 + 0.25V_{-1} + 0.13V_{-2} + 0.6V_{-3} \quad (9)$$

where Q_{base} is the base flow (2200 $m^3\ d^{-1}$ for Q_{surf} and 3350 $m^3\ d^{-1}$ for Q_{out}), V_0 is the volume of rainwater captured by the lake's catchment on the current day, V_{-1} is the volume captured on the previous day, etc. The 1-day half-life for the post-rainfall flow was derived from the response of the Aberjona river flow (as measured at the Upper Mystic Lake stream gauging station (*38*)) to rainfall (Boston, Logan Airport (*39*)). The rain volume was calculated by multiplying the rainfall depth by the effective catchment area, taken to be 0.4 km^2. The effective catchment area was adjusted to give the best fit to field observations of the flow. Seven-day averages of these calculated flows were used in the weeklong simulations. The high conductance flow, Q'_{high}, was found to follow the surface flows in the whole-lake mass balance calculations and therefore was set to 12% of Q_{out}. Q'_{high} varied over a small range in these simulations (410−570 $m^3\ d^{-1}$).

The depth of the epilimnion was changed throughout the 10 simulation periods to match field observations. The thickness of the metalimnion layer was set to 1 m for all simulations. The input concentrations of benzene and salt were taken from field data for the hypolimnion and surface inputs. When not available from field data, these values were estimated by interpolation. The water column concentrations were taken from field data *only for the start of the first simulation* (6/18/97 to 6/24/97). The input for each of the subsequent nine simulations was the output of the previous simulation.

Having set the flows and mixing behavior for these 10 weeks to fit the salt data, the benzene vertical profiles were modeled with the same parameter values and allowing biodegradation in the metalimnion. A single pseudo-first-order biodegradation rate constant (0, 1, 2, 4, or 8 d^{-1}) was applied for each temporal sequence over a 0.4 m zone centered either at 1.3 m (weeks 1−6) or 1.5 m (weeks 7−10).

Results and Discussion

Distribution of Benzene and Conductance in the HBHA. On 8/1/97 the horizontal distributions of conductance and benzene were examined at 0.6 and 2.5 m depths (see Supporting Information.) Two important trends were observed. First, the north-south gradients of conductance and benzene indicated that the high salinity, benzene-contaminated groundwater entered the HBHA at the northern end. At the location of groundwater inflow in the northern part of HBHA, 21 μM benzene and a conductance of 10.5 mS/cm were observed. This finding was repeated on 10/28/98 with 18 μM benzene and 12.5 mS/cm conductivity. The epilimnion in the northern part of the lake had low benzene concentrations (<0.2 μM) and low conductance (0.94 mS/cm). Moving from north to south, the disparity between the hypolimnion and epilimnion compositions was reduced. In the southern part of the lake, the hypolimnion had benzene concentrations ranging between 2.5 and 4.5 μM and a conductance of 4.2 mS/cm. This deep water was formed from previously exfiltrated, salty groundwater diluted by about a factor of 3 (Figure 2.) The epilimnion in the southern part of the lake had benzene concentrations of <1−25 nM and conductance of 1.1 mS/cm. The north-south gradients were consistent with a groundwater input in the northern part of the lake with subsequent dilution with epilimnetic water or fresher groundwater as the deep water flowed to the south.

The second important trend was the relative constancy of compositions found among stations in the southern basin of the lake. All of the sampling locations in the southern half of HBHA had similar epilimnetic and hypolimnetic conductances. Benzene concentrations in the southern half of the lake varied only little and were consistently below 1−10 nM in the epilimnion and between 3 and 3.3 μM in the hypolimnion. Because of this observed constancy, vertical profiles taken at Station A were presumed to be representative for the horizontal distribution of benzene and conductance in the southern part of HBHA on all other sampling dates.

Vertical Distribution of Benzene and Conductance at Station A. Due to the very high salinity of the groundwater discharge, the lake was stratified throughout the observation period (June 1997−January 1998) and a clear separation into an epilimnion of low conductance (550−800 μS/cm) and a hypolimnion of high conductance (2200−4400 μS/cm) was always observed (Figure 3.) Depths of the well-mixed, oxic epilimnion varied between 0.7 and 3.3 m. The profiles of benzene in the HBHA (Figure 3) were qualitatively similar to the conductance profiles—very high concentrations in the hypolimnion (from 2 to 5 μM at deepest part of the lake in the south) and very low concentrations in the epilimnion (ranging from 25 nM on 6/18/97 to below our detection limit, 1 nM on 7/1/97 and 8/14/97). The similarity of these profiles reinforced the conclusion that benzene and the salts contributing to the conductance (primarily Na_2SO_4, due to the historical use of NaOH and H_2SO_4 at Industri-Plex) originated from the same groundwater plume entering the lake at the north and were diluted similarly as they mixed during southerly flow. Further evidence for a common source comes from the close correlation ($r^2 = 0.89$, $n = 100$) between salt content and benzene concentration for all stations on all dates (Figure 4.)

While the benzene and conductance profiles were qualitatively similar, there were important differences. Although the shapes of the two profiles were similar in the hypolimnion, they diverged in the metalimnion. In the epilimnion, the benzene became quite low relative to salt. Some of the divergence can be accounted for by the fact that the benzene concentration was more affected by dilution than the conductance. This is because the diluting waters, which were mostly Halls Brook and low conductance groundwater, were essentially benzene-free but did have a significant conductance. Even after accounting for this, the epilimnetic benzene concentration was still lower than would be expected by dilution alone. These facts indicate that benzene was removed from the aqueous phase in the metalimnion or epilimnion.

Mass Balance Calculations: Establishing the Benzene Input (*I*). To establish the flux of benzene into the lake, a good estimate of the high-conductance groundwater flow was needed. Using the water flow and salt concentration data, we deduced that the flow of high conductance groundwater into the bottom of the lake, Q_{high}, was typically near 250 $m^3\ d^{-1}$. Davis et al. previously used seepage meters located down the center axis of the lake and found groundwater seepage rates near 20 $m^3\ d^{-1}$ for the Halls Brook Holding Area (*40*), considerably lower than the 250 $m^3\ d^{-1}$ that we calculate for the high-conductance groundwater input. Based on hydrologic modeling of groundwater-lake systems such as the HBHA and its surroundings (*41*) and on our own hydrographic observations, it is reasonable to expect that all of the high-conductance groundwater was exfiltrating into the HBHA near the lake's northern shoreline. The seepage

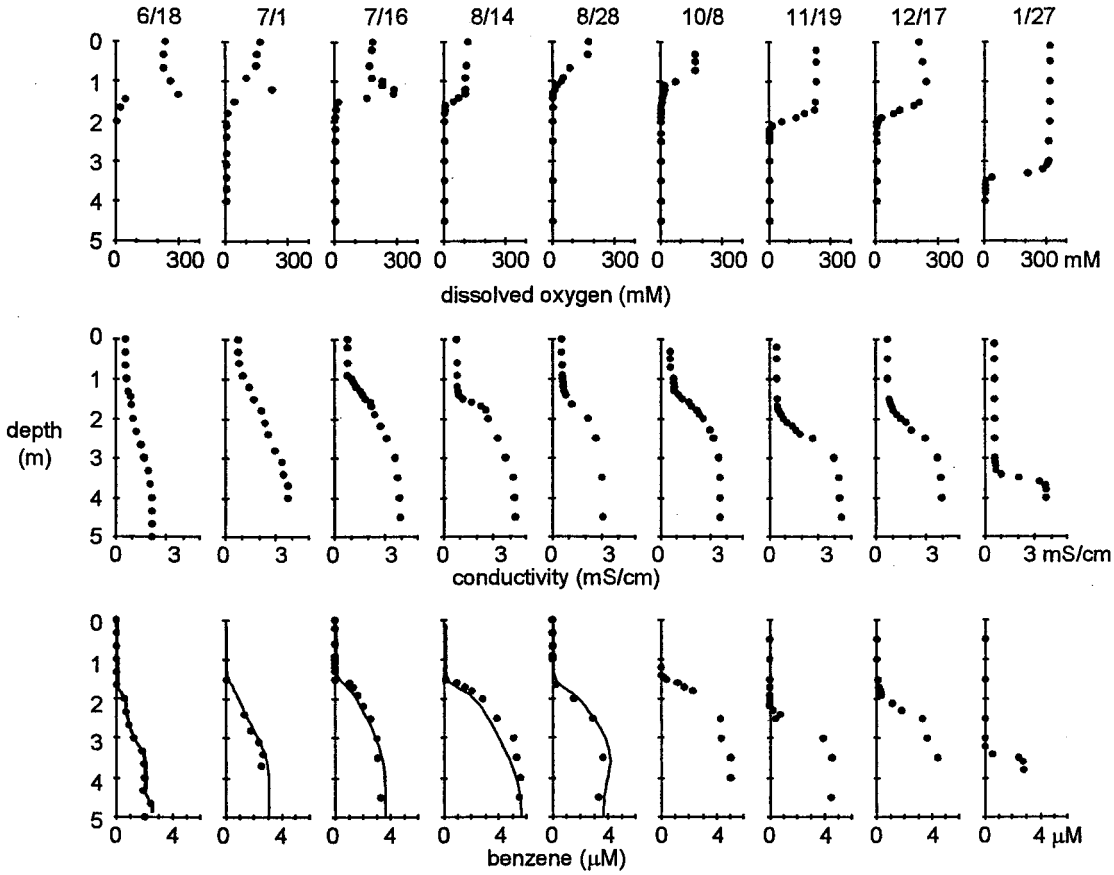

FIGURE 3. Depth profiles of dissolved of oxygen (DO) (top), specific conductance (middle), and benzene (bottom panels) at the deepest point of the HBHA (station A) on nine different days in 1997 and 1998. Lines through the summertime benzene profiles show fits by CHEMSEE modeling.

meters would not have recorded these flows. Hence, we conclude that Q_{high} had values near 250 $m^3\ d^{-1}$, and this was not in conflict with the lower exfiltration flows measured at the lake's centerline.

The high conductance groundwater was diluted by mixing with lower conductance lake water as it flowed from the north to the south along the lake bottom. Generally, we found that the resultant diluted flow, Q'_{high}, was about three times greater than Q_{high}. Upon filling the southern basin of the HBHA, the flow, Q'_{high}, supplied the upward advective "push" on the water column observed in the southern basin (Figure 2.)

Using these Q'_{high} results and our measures of benzene in the deep lake water, we calculated an average benzene input of 1.2 to 4.4 mol d^{-1} (Table 1). This contrasts sharply with the small amount of benzene observed to be leaving the HBHA through the outlet (ca. 0 to 0.5 mol d^{-1}). This immediately prompts the question what happened to most of the benzene.

Analysis of the Chemodynamic Behavior of Benzene in HBHA. Five removal processes for benzene were considered: water-to-air exchange, sedimentation, indirect photochemical transformation, episodic flushing, and biodegradation. The contribution of each pathway was estimated.

Water-to-Atmosphere Exchange. The volatilization rate (G) of benzene from the HBHA was calculated according to

$$G\left(\frac{mol}{d}\right) = A \cdot v_{tot} \cdot \left([C_6H_6]z{=}0 - \frac{[C_6H_6]_{air}}{K_H'}\right) \quad (10)$$

where A is the lake surface area, v_{tot} is the total transfer velocity, $[C_6H_6]_{z=0}$ and $[C_6H_6]_{air}$ are the surface water and air concentrations of benzene, and K_H' is the dimensionless Henry's constant (*35*). Given reported values of atmospheric concentrations of benzene in urban and suburban areas of major U.S. cities (0.5−3.6 ppbv) (*4*), one would expect that the air above the HBHA would serve as a sink of benzene. When air−water equilibrations were performed at HBHA, we found benzene in the water to be less than 1 nM, consistent with these reported air concentrations. Furthermore, no benzene (detection limit: <1 nM) was seen in surface water taken from a nearby suburban reference site (Upper Mystic Lake). These experiments indicate that the air concentrations of benzene are negligible compared with the aqueous concentrations.

The exposed lake surface area was 17400 m^2, except during two wintertime measurements when the HBHA was approximately half covered with ice ($A = 8700\ m^2$). The aqueous transfer velocities (v_{tot}) for benzene were estimated to be near 0.5 m d^{-1} given the region's average wind speed of 5 m s^{-1}. These calculations suggested volatilization rates were between <0.01 and 0.1 mol d^{-1} (Table 1), indicating that gas-exchange was an attenuation mechanism of secondary importance.

Sedimentation. The HBHA has a very high sediment deposition rate near 2 cm y^{-1} (*40*). We found that sediment collected near Station A exhibited 15% organic carbon contents and a porosity of 95%. These data imply an organic carbon flux to these sediments near 1 $g_{oc}\ m^{-2}\ d^{-1}$ or about 10 $kg_{oc}\ d^{-1}$ for the whole lake. With a K_{oc} of benzene near 100, if one assumes all this deposited organic matter is equilibrated with hypolimnetic water at about 2 μM, then about 0.002 mol benzene per day would be lost to the sediment bed. Obviously, this does not account for the missing benzene.

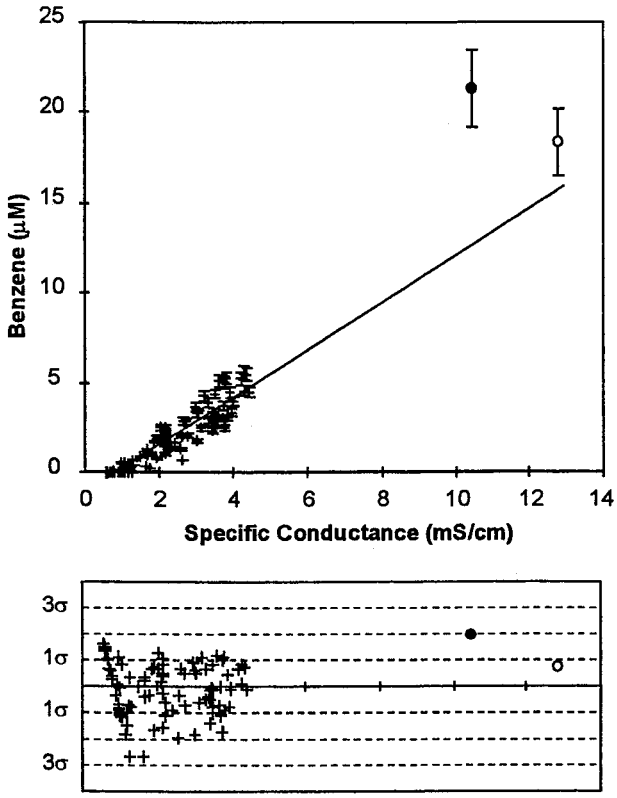

FIGURE 4. (Top panel) Correlation of measured conductance (mS/cm) and benzene concentration (μM) for all HBHA samples. Three data for which $|[C_6H_6]_{obs} - [C_6H_6]_{calc}| > 4\sigma$ were not included in the least-squares regression. For the remaining data (N = 100), the best fit line (y = mx + b) has $r^2 = 0.890$, m = (1.31 ± 0.05) × 10^{-3} (μM C_6H_6)(mS/cm)$^{-1}$, and b = −1.06 ± 0.11 μM. The error bars are assigned errors based upon a combination of representative replicate analyses and propagation of errors from dilution. (Lower panel) Residuals of the correlation represented as the number of standard deviations from the best-fit line.

Indirect Photochemical Transformation. Benzene does not undergo a significant direct photolysis in sunlight, since it does not absorb light at wavelengths >290 nm. However, a half-life of 16.9 days (*42*) has been reported for benzene in aerated, deionized water exposed to sunlight. This suggests indirect photolytic degradation may occur due to reaction of benzene with oxidants such as singlet oxygen or hydroxyl radical.

Using HBHA surface water on 8/21/96, the near surface [$^1O_2$] was determined to be 2.5 × 10^{-13} M. This result is consistent with the concentrations observed in Swiss eutrophic lakes by Haag and Hoigné (0.8−2.3 × 10^{-13} M for 10 ppm DOC) (*32*).

Together with a bimolecular rate constant of $k_{tot} = 2 \times 10^3$ M^{-1} s^{-1} (in CCl_4, (*43*)), a pseudo-first-order rate constant of 4 × 10^{-5} d^{-1} was calculated. Due to the high light attenuation in the surface water of HBHA (*31*), this reaction only applies to the uppermost water (ca. 2000 m^3) where the benzene concentrations are quite low (ca.1 nM). The benzene consumed by this mechanism therefore is negligible (ca. 10^{-8} mol d^{-1}).

Likewise, if one assumed an average near-surface hydroxyl radical concentration of 10^{-16} M (*35*) and a reaction rate constant of 7.8 × 10^9 $M^{-1}s^{-1}$ (*44*), then a pseudo-first-order degradation rate constant for benzene degradation of $k_{OH} = 0.07$ d^{-1} can be estimated. The small volume exposed to sunlight and the low benzene concentrations also make this an unimportant removal mechanism (ca. 10^{-4} mol d^{-1}).

Episodic Flushing. During the course of this study, periods of both high and low rainfall were observed. From a modeling standpoint, the lake was better behaved during the dry periods, with smoothly changing vertical chemical gradients. By contrast, the high rainfall periods were characterized by rapidly changing water column profiles. Large rain events were responsible for increasing the mixing in the upper part of the water column and for removing a substantial amount of the salt and benzene mass from the HBHA. These episodic flushing events were clearly a critical component of the mass balance, but were difficult to quantify a priori.

For the summer data in which storms were relatively infrequent, good agreement was obtained between the modeled and measured vertical profiles of salt concentration. The largest discrepancy was observed for the week ten profiles in which the predicted hypolimnion salt concentrations were much higher than observed. We postulated that this was due to imperfectly modeling the effect of four large rain events that occurred in weeks seven, nine, and ten. Empirically, we have observed increased mixing and flushing of the epilimnion during such rain events. To simulate this effect, the initial profiles for weeks seven, nine, and ten were set to 600 μS/cm for the upper part of the water column (1.6 m for weeks seven and nine, and 2.0 m for the largest event in week ten). This modification gave a final week ten profile that was in better agreement with the field observation.

We estimated the magnitude of rain flushing by considering the effect of replacing the upper 2 m of the water column with water that had a conductance of 600 μS/cm (1.6 mM Na) and no benzene. There were fifteen rain events capable of at least this amount of flushing over the course of this 223-day study. Averaging over the entire time, these events caused a daily average loss of benzene of 0.0−1.4 mol d^{-1} (Table 1).

It is interesting to consider the potential for episodic downstream releases of benzene due to this mechanism. In the worst-case scenario, the lake's benzene inventory would be at the high end (60 mol benzene) and a rainfall would produce mixing of the upper 2 m of the water column (30,000 m^3). This would result in approximately 6 mol benzene in 30,000 m^3 (16 ppb) or about 10 times the concentration normally observed and three times the federal drinking water limit. Of course, the concentration of benzene would likely be greatly attenuated during transport downstream through volatilization and potentially biodegradation.

Microbiological Degradation. Having ruled out other likely mechanisms, we hypothesized that microbially mediated degradation was the primary sink for benzene in the HBHA. First, the vertical profiles of benzene in the water column indicated that this compound was consumed at the depth where the benzene-rich bottom waters met the oxic epilimnion. These profiles were consistent with the presence of a benzene-degrading microbial population residing in the metalimnion. The oxic-anoxic interface in the metalimnion was thought to be an ideal location for the biodegradation because there were high substrate concentrations, significant oxygen content, and a low hydrodynamic turbulence that would allow the formation of stable bacterial communities.

Additionally, we were able to support this hypothesis using laboratory incubations of HBHA water. Samples taken from the metalimnion that contained both benzene and oxygen always displayed benzene degradation (Figure 5). Fitting all data following initial removal trends, these data implied pseudo-first-order degradation rates between 1 and 2.5 d^{-1}. We note that the two metalimnetic samples that showed cessation of benzene removal after about 5 h were initially very low in DO. Of the two samples taken from the epilimnion, one showed a measurable degradation of benzene (1 d^{-1}), while the other showed <0.1 d^{-1}. The anoxic sample taken from the hypolimnion displayed degradation below 0.04 d^{-1}.

TABLE 1. Benzene Mass Balance Components

		sources groundwater		sinks					
				outflow			episodic flushing		
date	$d(C_6H_6)/dt$ (mol d^{-1})	$[C_6H_6]_{St.A.}$ (mM)	I (mol d^{-1})	$[C_6H_6]_{out}$ (mM)	O (mol d^{-1})	volatility G (mol d^{-1})	no. of events	F (mol d^{-1})	biodeg B (mol d^{-1})
7/1/97	0.93	3.4	3.1	<0.002	<0.007	<0.023	0	0.00	2.2
7/16/97	0.81	3.4	1.5	0.013	0.044	0.11	0	0.00	0.5
8/14/97	0.82	5.5	4.1	<0.002	<0.013	<0.019	1	0.14	3.1
8/28/97	−1.76	3.3	2.3	0.006	0.020	0.048	3	1.36	2.7
10/8/97	0.56	5.1	1.2	<0.002	<0.007	<0.014	0	0.00	0.6
11/19/97	−1.76	4.5	1.9	0.004	0.036	0.035	5	0.74	1.9
12/17/97	0.47	4.5	3.3	0.020	0.18	0.077	1	0.10	2.5
1/27/98	−0.81	2.8	4.4	0.019	0.51	0.089	5	0.50	4.1

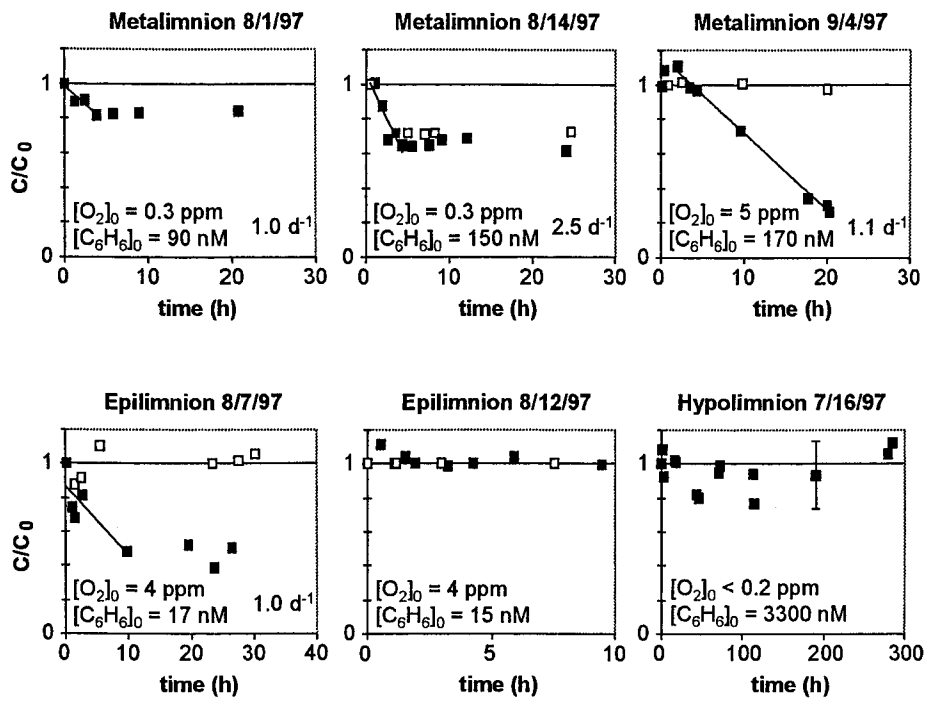

FIGURE 5. Changes in benzene concentration over time (normalized to initial benzene concentrations) in laboratory incubations of water taken from the HBHA (initial benzene and DO levels shown on each time course). The filled symbols correspond to the untreated samples. The open symbols correspond to filtered controls for the epilimnion waters and to metalimnetic waters dosed with NaN3, HgCl2, chloramphenicol, and tetracycline. Lines indicate initial rate coefficients determined by least-squares regression.

These experiments support the notion that the primary location of biodegradation was the metalimnion and that biodegradation in the hypolimnion was much slower or absent altogether. This does not completely rule out the occurrence of biodegradation in the hypolimnion, since even slow transformation rate could prove important over the long (ca. 100 day) residence time. However, the tight relationship of conductance and benzene concentration (Figure 4) did not support a hypolimnetic sink for benzene.

To support the hypothesis that we were observing biodegradation, we examined the ability of water filtration and poisons/antibiotics to inhibit benzene removal in laboratory incubations (Figure 5, open symbols.) Filtered epilimnetic samples exhibited no benzene losses. Metalimnetic water, dosed with $HgCl_2$, NaN_3, chloramphenicol, and tetracycline on 9/4/97 did not show significant benzene loss over 24 h. We did still see significant decrease of benzene in the 8/14/97 sample, however. It is possible that the poisons/antibiotics were added at ineffective levels or their activities were reduced due to interactions with other water constituents. The filtration and poisoning/antibiotic results appear consistent with a biodegradation mechanism.

Using the laboratory incubation experiments as a guide, we estimated a whole-lake biodegradation sink. To this end, we used the pseudo-first-order rate seen in the laboratory incubations of between 1 and 2.5 d^{-1}. Assuming an average metalimnetic benzene concentration of 0.3 μM and a metalimnion volume of 4000 m^3 (i.e., using a cross sectional area of 10,000 m^2 and a 0.4 m layer thickness), we can multiply the degradation rate times the mean concentration times the volume to estimate a whole-lake benzene sink. The result is between 1.2 and 3 mol d^{-1}. A similar calculation for the epilimnion suggests that this surface layer may support some of the biodegradation occurring in the HBHA (0.04 mol d^{-1}), but it is of secondary importance. This estimate for the metalimnion is comparable to the rates of benzene input and strongly supports the hypothesis that biodegradation was the major sink for benzene in the HBHA.

CHEMSEE Modeling of Temporally Evolving Benzene Profiles in the HBHA. A one-dimensional computer model was used to assess whether the temporally evolving vertical profiles of benzene, observed on a succession of dates from Station A, could be fit using the pseudo-first-order biodegradation rate obtained in the laboratory incubations. To

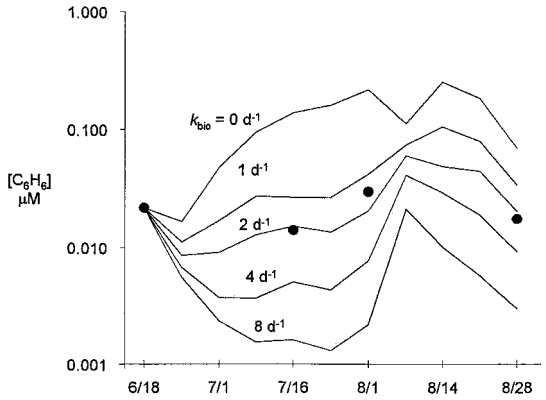

FIGURE 6. Predicted changes in epilimnion benzene concentrations for the summer of 1997 from CHEMSEE computer simulations (lines) using five different metalimnion biodegradation rate constants (0, 1, 2, 4, and 8 day^{-1}). Measured benzene concentrations from epilimnion field samples (circles) correspond best with the 2 d^{-1} rate coefficient.

model the benzene profiles, sedimentation and photochemical transformations were assumed to be unimportant (vide supra). The high-conductance groundwater was taken to be the sole source of benzene. We assumed no biodegradation within the hypolimnion. The elimination of benzene in the metalimnion was modeled to take place at a thin, 0.4 m thick layer at the oxic-anoxic interface. The benzene concentration in the epilimnion, $[C_6H_6]_{epi}$, which was a measure of how much benzene passed through the metalimnion, proved to be a sensitive parameter to assess the model's sensitivity to the different biodegradation rate constants (Figure 6). With no biodegradation, the simulations indicated that $[C_6H_6]_{epi}$ should steadily rise, decreasing only after major rain events. With a pseudo-first-order rate constant of 2 day^{-1}, a relatively constant $[C_6H_6]_{epi}$ was observed in the simulations, whereas larger rate constants (4 and 8 day^{-1}) resulted in steadily decreasing $[C_6H_6]_{epi}$. Field observations suggest a relatively constant $[C_6H_6]_{epi}$ of 10^{-2} μM and therefore strongly supported a metalimnion-specific rate of $k_{bio} = 2$ d^{-1}.

Significance. This study has shown that the largest sink of benzene in the HBHA was biodegradation at the oxic-anoxic interface within the lake. The fact that the benzene-contaminated groundwater plume is being captured and largely degraded by a down-gradient eutrophic lake suggests that such stratified water bodies may serve as engineered solutions to groundwater contamination. However, it is important to point out that this naturally occurring bioreactor is also susceptible to disturbance by rainstorms. These episodic events undoubtedly elevate the surface concentrations of benzene and cause releases of this toxic chemical downstream.

This study provided evidence that short-term laboratory incubations *of the appropriate samples from a heterogeneous field site* can give a reasonable values for the in situ biodegradation rate. Laboratory incubations provided a pseudo-first-order rate between 1 and 2.5 day^{-1}. Whole-lake mass balance calculations and computer simulations were in strong agreement as they indicated that the actual rate in a key subportion of the lake was approximately 2 day^{-1}. Now we need to learn to predict such localized rates for situations of interest.

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Supporting Information Available

Table S1 (horizontal distribution of conductance and benzene [8/1/97]), Table S2 (parameters used in the CHEMSEE modeling simulations), Table S3 (flow and conductance measurements for the flows of the HBHA), and Figure S1 (map of HBHA showing 8/1/97 sampling locations). This material is available free of charge via the Internet at http://pubs.acs.org.

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