The production of chemical heterogeneity in Upper Mystic Lake

K. Knauer, H. M. Nepf,[1] *and H. F. Hemond*

R. M. Parsons Laboratory, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Abstract

Chemical heterogeneity in a lake may arise from spatially and temporally nonuniform inputs or from spatially nonuniform transformation rates within the water body. The potential for heterogeneity to persist at a given spatial scale then depends on the relative magnitudes of the hydraulic residence time, the timescale for mixing, and the timescale for transformations to and from the chemical species of interest. Through simple scaling arguments, the potential for heterogeneity in total arsenic (As) and arsenic speciation were predicted for Upper Mystic Lake, a small urban lake near Boston, Massachusetts. Specifically, heterogeneity in total arsenic was expected during periods of high inflow—which are typical of spring conditions—given a sufficient magnitude of inflow variation. Heterogeneity in As(III) was expected throughout the year, whenever spatial variations in the net As(V)-to-As(III) transformation rate exceeded a few percent per day. Observed heterogeneity was consistent with these predictions. Although modest, heterogeneity in total As was highest in early spring (7%, expressed as the spatial standard deviation divided by the lakewide mean). By contrast, heterogeneity of As(III) was as high as 36%, indicating that spatial variation in oxidation and reduction rates is sufficient to contribute to heterogeneity. Heterogeneity in As(III) varied significantly from month to month.

Chemical studies in small lakes are frequently conducted under the tacit assumption that epilimnetic waters are horizontally well mixed, at least in the limnetic zone. Under that assumption, water profiles are measured at a single site, and the chemical properties of that station are considered to be representative of the entire lake. Spatial variance of chemical properties could introduce errors into such one-dimensional studies. Spatial heterogeneity, or patchiness, has long been recognized in biological populations such as phytoplankton (*see,* for example, Platt et al. [1970]; Steele [1974]), and its occurrence has been attributed to combinations of organismal behavior (e.g., predator–prey interactions) and physical processes (e.g., fronts, seiches). Feedback between water chemistry and growth rates may also produce heterogeneity in water chemistry. Even in the absence of biology, chemical heterogeneity can arise from (1) chemical differences between lake water and stream inflow and (2) local production or consumption of chemical constituents within the lake. Whether heterogeneity persists depends on the rate at which it is produced by transformation and/or inflow relative to the rate at which it is destroyed through mixing.

Upper Mystic Lake (UML) is an urban lake in eastern Massachusetts. We hypothesized that heterogeneity in arsenic (As) speciation is a regular feature of UML based on the observations of Trowbridge (1995), who found on two of four sampling dates that the epilimnetic concentration of reduced As [As(III)] varied significantly among three stations along a north–south transect. The total As concentration was not observed to vary along this transect. Furthermore, Spliethoff (1995) observed unexpectedly large transforma-

tion rates for As(V) to As(III), which could facilitate patchiness in As(III), as discussed later. In the present study, we test the hypothesis that various As pools exhibit spatial variability within UML, and we consider both inflow variability and internal As transformation as possible causes.

Characterization of spatial heterogeneity is important to lake studies for several reasons. It may be necessary to account for heterogeneity when designing limnological experiments or sampling strategies. The identification and characterization of patchiness provides insight into the dynamics of aquatic ecosystems; for example, an observation of heterogeneity coupled with a knowledge of mixing rates establish bounds on the possible range of relevant transformation rates. Finally, heterogeneity in contaminant or pathogen distribution complicates estimates of human exposure and risk assessment.

Background

As transformation rates—The net reduction rate of As is observed to be in the approximate range of 10^{-9} to 10^{-8} mol L^{-1} d^{-1} for the epilimnetic waters of UML (Table 1). In this aerobic environment, reduction may serve as a detoxification mechanism (e.g., Knauer et al. 1999) and is likely to be adenosine triphosphate–dependent and mediated by a system such as the well-documented *ars* system (e.g., Broer et al. 1993; Silver 1997). Although it is sometimes assumed that phytoplankton are primarily responsible for As reduction in oxic waters, Spliethoff (1995) has reported significant net As reduction in 0.45-μm–filtered UML water, indicating that free-living bacteria can also be important. Net oxidation rates of similar magnitude have been observed in natural freshwaters, and both microbial and abiotic (e.g., photooxidation) oxidation processes may be important (Scudlark and Johnson 1982; Maeda 1994; *see Table 1*). As in the case of reduction, As oxidation rates are usually measured as net

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Table 1. Reported arsenate reduction and oxidation rates.

Reduction rates	Organisms or system	Reference
6.7×10^{-9} mol L^{-1} d^{-1}	*Skeletonema costatum* (marine diatom)	Sanders and Windom (1980)
$0.0–1.6 \times 10^{-9}$ mol L^{-1} d^{-1}	Spring Bloom, UML, 1992	Aurilio et al. (1994)
$0.0–1.6 \times 10^{-9}$ mol L^{-1} d^{-1}	Spring bloom, UML, 1997	This study
$0.0–1.6 \times 10^{-9}$ mol L^{-1} d^{-1}	Summer bloom, UML, 1997	This study
$0.1–1.0 \times 10^{-8}$ mol L^{-1} d^{-1}	UML, 1995	Spliethoff (1995)
$2.4–8.4 \times 10^{-7}$ mol L^{-1} d^{-1}	Spiked lake water	Spliethoff (1995)
$0.3–2.0 \times 10^{-9}$ mol L^{-1} d^{-1}	*Chlorella* sp. cultures	Knauer and Hemond unpubl. data
Oxidation rates		
$0.7–3.0 \times 10^{-10}$ mol L^{-1} d^{-1}	Autumn, UML, 1992	Aurilio et al. (1994)
$0.7–3.0 \times 10^{-10}$ mol L^{-1} d^{-1}	Spring, UML, 1997	This study
1.0×10^{-6} mol L^{-1} d^{-1}	Lake Ontario	Scudlark and Johnson (1982)
8.9×10^{-7} mol L^{-1} d^{-1}	Cazenoria Lake	Scudlark and Johnson (1982)
3.5×10^{-9} mol L^{-1} d^{-1}	Seawater	Scudlark and Johnson (1982)
2.8×10^{-9} mol L^{-1} d^{-1}	Seawater	Johnson and Pilson (1975)
3.2×10^{-10} mol L^{-1} d^{-1}	Seawater	Peterson and Carpenter (1983)
1.2×10^{-9} mol L^{-1} d^{-1}	Marine algae	Sanders (1978)
4.75×10^{-11} mol L^{-1} d^{-1}		Howard et al. (1984)

UML, Upper Mystic Lake.

rates and may reflect a difference between oxidation and reduction kinetics.

For comparison with the physical timescales discussed below, the appropriate timescale for As redox transformations is k^{-1}, where k is the observed rate divided by the mean concentration; this corresponds to a first-order rate constant if first-order kinetics are assumed. In UML, a typical reduction rate of 1 nmol L^{-1} d^{-1} corresponds (approximately) to $k = 0.03$ d^{-1}; however, rates as high as 10 times this value have been observed in UML (Table 1). Note that only spatially nonuniform transformation rates produce heterogeneity and that variation is expected to be of the same order of magnitude as the mean rate.

Mixing rates in lakes—Two timescales are used to assess the potential role of physical processes in creating or destroying heterogeneity. First, the nominal residence time of the surface layer, T_{res}, is

$$T_{res} = \frac{Ah}{Q},\qquad (1)$$

where h is the surface-layer depth, Q is the inflow, and A is the surface area of the lake basin. Second, the timescale required to mix the surface layer to uniformity in the horizontal is

$$T_{mix} = \frac{A}{D},\qquad (2)$$

where D is the horizontal diffusivity. The horizontal diffusivity increases both with turbulence intensity, which in the epilimnion is strongly correlated to wind speed, and with the eddy scale contributing to the turbulent diffusion. Typically, many eddy scales coexist, and they range from centimeter sized to basin-scale gyres, but only those scales that are comparable to or less than the patch size can contribute to its dispersion. Thus, as a patch grows as a result of turbulent diffusion, larger eddies contribute to its diffusion, and the

rate of diffusion increases. This scale dependence has been demonstrated for scales of 10 to 10^5 m (Lawrence 1995; Okubo 1971). In Eq. 2, D must be based on the characteristic eddy scale that makes the greatest contribution to homogenization at the basin scale. In UML, which has a length scale of $\sqrt{A} \approx 1,000$ m, the epilimnion is principally homogenized by eddies of 100-m scale. Smaller eddies produce much slower rates of diffusion, and larger eddies contribute only to stirring (advection). Using the experimentally supported scale dependence (George and Allen 1994; Lawrence 1995), the corresponding diffusivity is 0.05–0.1 m^2 s^{-1}.

The ratio of Eqs. 1 and 2 is a form of the Peclet number:

$$Pe = \frac{T_{mix}}{T_{res}} = \frac{Q}{Dh}\qquad (3)$$

which describes the relative importance of mixing and advection within the surface layer. For conditions of $Pe > 1$ ($T_{res} < T_{mix}$), advective processes control the distribution of water-quality constituents and may produce heterogeneity. Under these conditions, varying inflow concentration can create heterogeneity within the surface layer. For example, storm events affect As concentration in the Aberjona River, which feeds UML (Solo 1995), such that storm inflow is chemically distinct from the surface layer. Differential heating between the forebay and main basin (*see Fig. 1*) may also produce heterogeneity by creating exchange flows that carry As-rich forebay water into the surface layer of the lake (Nepf and Oldham 1997). Under either condition, the timescale of inflow variation dictates the spatial scale of heterogeneity produced in the lake and thus its potential persistence. Diapycnal fluxes of chemically distinct hypolimnetic water may also create patches within the epilimnion and contribute to increases in total epilimnetic concentration. However, localized settling and scavenging seem unlikely to be of sufficient magnitude to produce observable heterogeneity. In contrast, when $Pe < 1$ ($T_{mix} < T_{res}$), diffusion has sufficient time to erase heterogeneity introduced by the advective
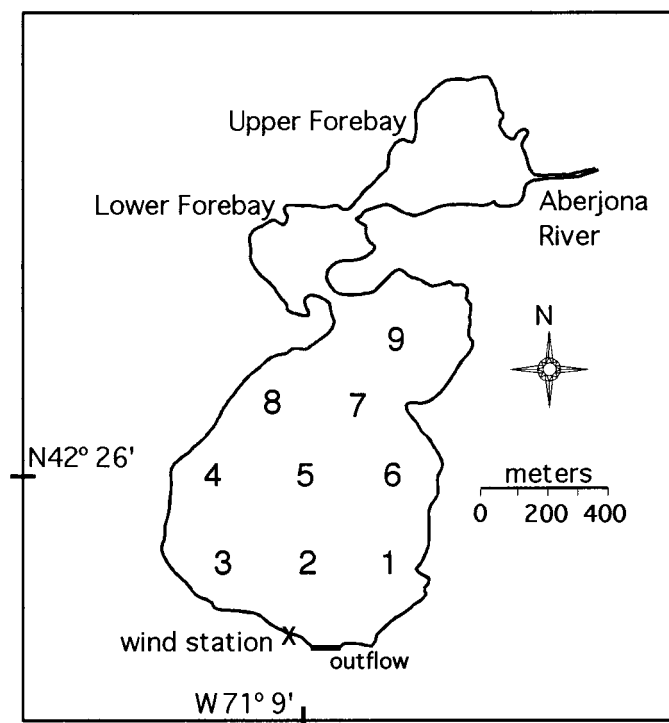
Fig. 1. Upper Mystic Lake near Winchester, Arlington, and Medford, Massachusetts, showing inlet, shallow forebays, and sampling locations. The lake stations are located on a 300-m grid.

processes described above, thereby promoting a homogeneous surface layer.

Chemical transformation can also produce heterogeneity of a given chemical species if the timescale for transformation, k^{-1}, is short compared to the dominant transport timescale. The ratio of transport and transformation timescales is a Damkohler number, Da, which is defined differently under advection ($Pe > 1$) and diffusion-dominated ($Pe < 1$) regimes.

$$Pe > 1 \rightarrow Da = \frac{T_{res}}{k^{-1}} = \frac{kAh}{Q} \qquad (4a)$$

$$Pe < 1 \rightarrow Da = \frac{T_{mix}}{k^{-1}} = \frac{kA}{D} \qquad (4b)$$

Lake-scale heterogeneity is expected when $Da > 1$. Heterogeneity at smaller scales can also be predicted from Eq. 4 by replacing the lake scale, $\sqrt{A}$, with the scale of interest. For example, chemical patches of dimension L may arise in a diffusion-dominated regime if $Da = kL^2/D > 1$. From this condition, one can estimate the variation in transformation rate required to produce heterogeneity among sampling locations spaced a distance L apart, as follows:

$$k > \frac{D}{L^2} \qquad (5)$$

In the case of UML, sampling stations were 300 m apart ($L = 300$ m). Using Eq. 5 and the estimated diffusivity, local amplification of k greater than 0.05–0.1 d^{-1} (relative to a

mean value) would be required to generate patchiness at the spatial resolution of the observations. Because rates of this magnitude are likely (*see Table 1 and discussion above*), heterogeneity was expected to occur at the sampling scale. Because the actual patch scale may be smaller than the station spacing, Eq. 5 is a lower bound for the transformation rate needed to produce heterogeneity at the sampling scale. If the patch scale is greater than the station spacing (i.e., patches span two or more adjacent stations), then the observed patch scale may be used for L in Eq. 5 to yield a more accurate lower bound on k.

Methods

Study site—UML is located near Boston, Massachusetts (Fig. 1). The main basin has a surface area of 45 ha, a volume of 7×10^6 m^3, a mean depth of 15 m, and a maximum depth of 24 m. Stratification develops in early summer, resulting in hypolimnetic anoxia (Aurilio et al. 1994). UML drains the historically contaminated Aberjona Watershed, containing Environmental Protection Agency Superfund and other contaminated sites that harbor a large inventory of As and other toxic metals (Durant et al. 1990; Aurilio et al. 1995).

Sampling—Water samples were collected in duplicate at the mid-depth of the epilimnion from nine stations in the lake and from the channel connecting UML with its forebays (Fig. 1). Samples were collected monthly from April to September (May to September at the inflow). At most, 3 h were required to sample the 10 stations. A much longer amount of time is required for mean advection or wind-drift to carry water masses between the station locations, O(1 d), or for turbulent diffusion to mix water between stations, O(10 d), confirming that samples represent distinct water masses at approximately synoptic times. The sampling time is also much shorter than typical transformation time scales, O(10 d).

At each lake station, water was pumped from 3-m depth (1.5-m depth at the inflow) into acid-washed polyethylene bottles using a peristaltic pump with acid-washed vinyl tubing. Sample bottles were flushed two times before filling and were maintained on ice in the dark until they were analyzed. Each sample was divided into subsamples for As speciation and chlorophyll a (Chl a) measurements. Subsamples of each bottle for total As measurement were acidified; other aliquots were filtered through an acid-washed 0.45-μm filter to determine the total filterable As concentration (afterward referred to as As dissolved) and the amount of As present as As(III).

As speciation and Chl a determination—The concentrations of total As and total dissolved As were determined by inductively coupled plasma mass spectrometry (Perkin-Elmer Sciex Elan 5000). The detection limit for As was 10^{-9} M. Analysis of dissolved As(III) was completed within 1 d of sampling using a continuous hydride generation system and atomic fluorescence detector (Questron "Excalibur"). For selective hydride formation from As(III), samples were maintained at pH 5.0 during the hydride reaction with TRIS

buffer (Andreae 1977; Aurilio et al. 1994). Blank values were lower than the detection limit ($<5 \times 10^{-10}$ M). Standards were made from stock solutions (SPEX chemicals). Concentrations of As(V) were calculated from the difference between total dissolved As and dissolved As(III). Lake-averaged net reduction/oxidation rates were estimated from the difference in mean lake concentration among successive sampling dates. Changes in both As(III) and As(V) were considered to produce two estimates of the net rate. These estimates assume that changes in concentration arise only through transformation between As(III) and As(V), neglect inflow, and assume that the period between sampling is shorter than the residence time, such that the same water mass is sampled. For Chl *a* measurements, subsamples of 1,000 ml ($N = 2$, one from each sampling bottle) were passed through GF/F filters, which were then extracted in ethanol prior to spectrophotometric determination of Chl (Meyns et al. 1994 and references therein).

Physical measurement—Continuous hourly measurements of river flow, $Q(t)$, were recorded at the United States Geological Survey gauging station located on the Aberjona River, 800 m upstream of the upper forebay of the UML (Fig. 1). Continuous wind speed and direction were recorded at 10-min intervals from a 10-m flagpole located at the southern end of the lake. Profiles of temperature made throughout the season with a HydroLab conductivity temperature depth (CTD) probe were used to estimate h, the depth of the surface layer.

Heterogeneity index—We define a heterogeneity index (HI) as a measure of the spatial heterogeneity of a chemical species at a given time, thus:

$$HI = \frac{\sqrt{S_s^2 - S_m^2}}{\text{mean concentration of chemical}} \times 100\%, \quad (6)$$

where S_s is the standard deviation among measured concentrations at the nine stations within the lake. The technical error, S_m, is a correction for the component of S_s attributable to analytical variability. It is assumed in Eq. 6 that analytical variability and spatial variability add in quadrature. The technical error is calculated by

$$S_m = S_r/\sqrt{2}, \quad (7)$$

where S_r is the standard deviation expected for repeated analyses of the same water sample. For each sampling date, S_r is calculated from the differences between duplicate samples at each station (Peters et al. 1974),

$$S_r^2 = \sum_{i=1}^{9} \sum_{j=1}^{2} (x_{i,j} - \bar{x}_i)^2/9, \quad (8)$$

where $x_{i,1}$ and $x_{i,2}$ are the measurements at Sta. *i*, and where $\bar{x}_i = (x_{i,1} + x_{i,2})/2$. Note that S_r and S_m would be zero if each analysis agreed perfectly with its duplicate, regardless of any difference from station to station. Equation 6 is reasonable when the spatial heterogeneity, S_s, is much larger than the technical error, S_m. However, when these values are comparable, the estimated spatial heterogeneity may largely be an expression of technical error, with the true spatial hetero-
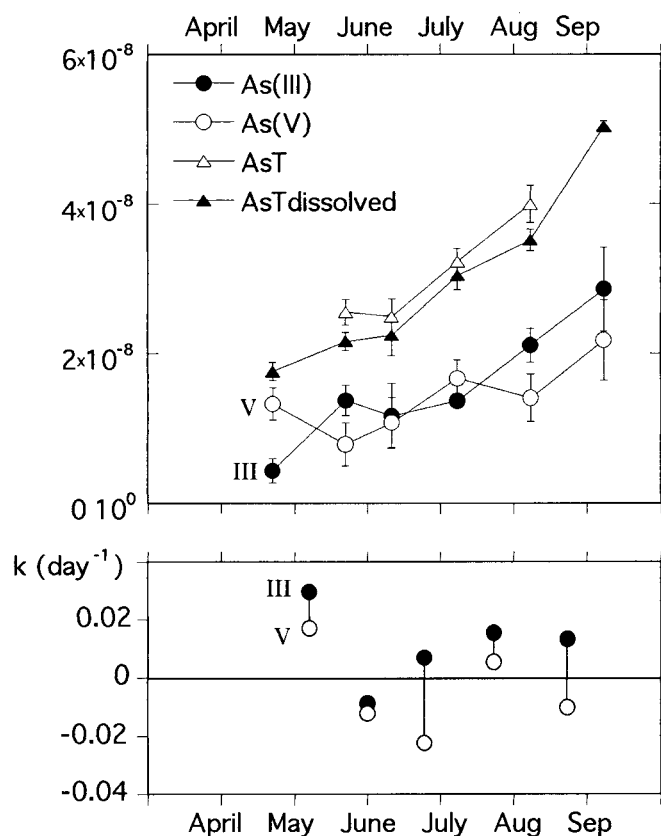

Fig. 2. Lake mean arsenic (As) concentrations in UML during 1997, averaged over Sta. 1–9 (upper panel). Lower panel shows net transformation rate that, if constant throughout the interval, would be sufficient by itself to account for the observed change in lake average As(III) (closed symbol) or in lake average As(V) (open symbol). Total dissolved As is As filtered through an 0.45-μm filter.

geneity being uncertain but possibly significantly smaller. For such cases, we took S_m/mean concentration to be an upper limit on HI.

As(III) concentration is plotted at station locations in Fig. 4. Stations are highlighted if the concentration, $\bar{x}_i$, falls outside the 95% confidence limit for variance associated with analysis error (i.e., outside the interval $[\bar{x} \pm t(S_m)]$), where $\bar{x}$ is the lake mean concentration and $t = 2.3$ (i.e., $P = 0.05$, df = 8). High values are marked by a rectangle, and low values are marked by an oval. The number and location of highlighted values provide a visual assessment of the presence and spatial distribution of heterogeneity.

Results

Epilimnetic total As and total dissolved As concentrations trended upward during the study period, and As(III) increased both in absolute concentration and as a fraction of total As (Fig. 2). Reduction rates estimated from these trends (Fig. 2, lower panel) are consistent with the order of magnitude obtained in previous studies (0.03 d^{-1}; Table 1).

The HI for total dissolved As was highest at the April measurement (7%), declining to 5% or less for the remaining months. A similar pattern was found for the three dates on
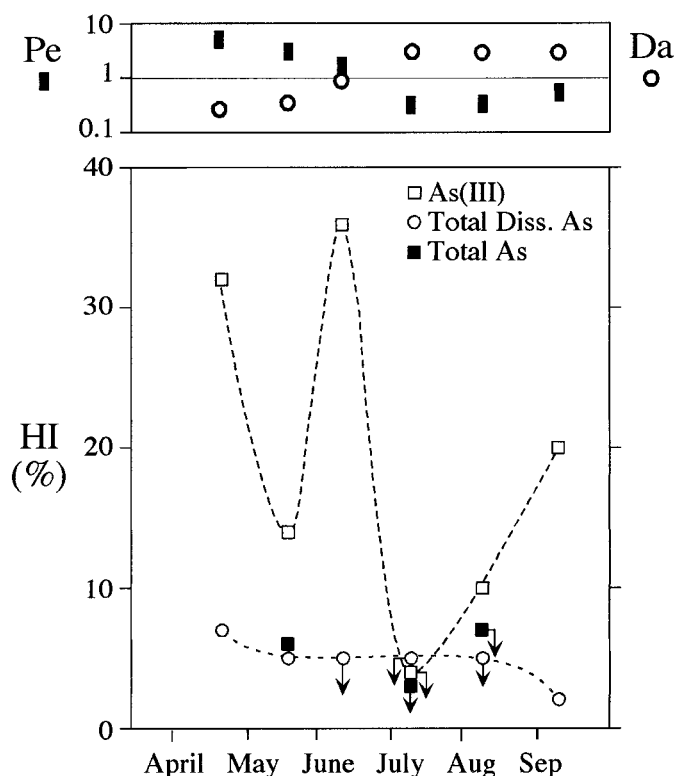
Fig. 3. Heterogeneity index (HI) for arsenic (As)(III) and total As in UML in 1997. A downward arrow indicates that the estimate should be taken as the upper limit for HI because S_s is not large relative to S_m (*see text*).

which total (unfiltered) As and its analytical error were measured (Fig. 3). HI was much larger for As(III), reaching its highest value of 36% in June (Fig. 3) and averaging in excess of 19% for the 6 months. At each date, except the July date, our criterion for calculation of a specific value of As(III) HI was met. In July, we estimated an upper bound on the HI of 4%.

Chl *a* averaged 4.7 μg L^{-1} and was highest (>6.5 μg L^{-1}) in April, August, and September. The HI for Chl *a* was higher, on average, than it was for As species, averaging 24% over the six dates (individual data not shown). Neither Chl *a* concentration nor its HI appeared to be correlated with corresponding values for As(III). Although a correlation between Chl and As(III) concentration or HI might be expected, its absence is not surprising for several reasons, including the following: different reduction rates by different phytoplankton species (e.g., Knauer et al. 1999); a significant role for heterotrophic bacteria (which, although probably stimulated by phytoplankton production, would likely exhibit lags following phytoplankton blooms); or the probable occurrence of oxidation concurrent with reduction, such that gross reduction is not the sole determinant of net reduction rate.

The seasonal trends in physical forcing and the timescales derived from them are shown in Table 2. As the mean inflow, $\bar{Q}$, decreased from April to August, the nominal residence time, T_{res}, increased from 14 to 190 d. The standard deviation of the flow, σ_Q, is an indicator of storm intensity, which decreased over the study period. The mean wind speed, $\bar{W}$,

and gustiness, σ_W, are both higher during the spring months. Estimates of Wedderburn number, based on wind speed and water temperature structure (*see,* for example, Imberger and Patterson 1990), indicate that upwelling events were not prominent throughout the sampling period, but less-pronounced seiche-induced diapycnal transport may have been present. The lake-scale mixing time, T_{mix}, is given for the high and low estimated diffusivities. Because turbulent diffusivity is enhanced by wind-induced turbulence, one could reasonably associate the higher diffusivity (0.1 m^2 s^{-1}) and the minimum mixing time of ~50 d with months of higher wind speed and gustiness. For both values of diffusivity, however, a clear relative trend between T_{res} and T_{mix} is apparent. Specifically, $T_{res} < T_{mix}$ ($Pe > 1$) during the first 3 months, indicating that physical processes permit heterogeneity if inflow variations occur and that chemically or biologically distinct parcels of water physically introduced into the lake may traverse the lake before being erased by mixing. In July through September, however, $T_{res} > T_{mix}$ ($Pe < 1$), indicating that physical processes promote homogeneity even if chemical variation in the inflow occurs. Finally, the Damkohler number (Table 2) indicates that the contribution of transformation to the generation of patches increases through the summer season.

Discussion

The measurements made in this study were designed to test for the existence of heterogeneity in arsenic concentrations and to suggest the physical and chemical processes that have sufficient magnitude to produce heterogeneity. Heterogeneity is expected to arise from inflow variation when two conditions are met. First, the inflow must have a chemically distinct, time-varying signature. Second, for the patches to persist, the timescale required to erase them (T_{mix}) must be longer than the residence time within the lake (T_{res}) (i.e., $Pe > 1$). In UML, the Peclet number steadily declined from April through August 1997, indicating that conditions within the lake shifted from those that favored heterogeneity due to inflow variability ($Pe > 1$) to those that favored homogeneity even in the presence of inflow variability ($Pe < 1$). This Pe trend is reflected in the total As HI, which decreased from April to September (Fig. 3). However, the index remained at or below 7% throughout the season, indicating that heterogeneity of total As is not a prominent feature in UML. This may be attributed to a lack of inflow variation (i.e., the first condition for physical patchiness is not met or is met only weakly).

The HI for As(III) generally exceeds that for total As by a substantial margin, indicating that an additional source of heterogeneity (e.g., spatially nonuniform transformation) contributes to the patchiness of this species (although inflow variations may also be proportionately larger than for total As). The seasonal trends in As(III) HI were also more complex, decreasing and increasing throughout the growing season. The As(III) heterogeneity was highest in June, with HI = 36%. On this date, the inflow concentration exceeded mean lake concentration (18.7 vs. 11.7 nM, respectively), and the highest As(III) concentrations in the lake occurred
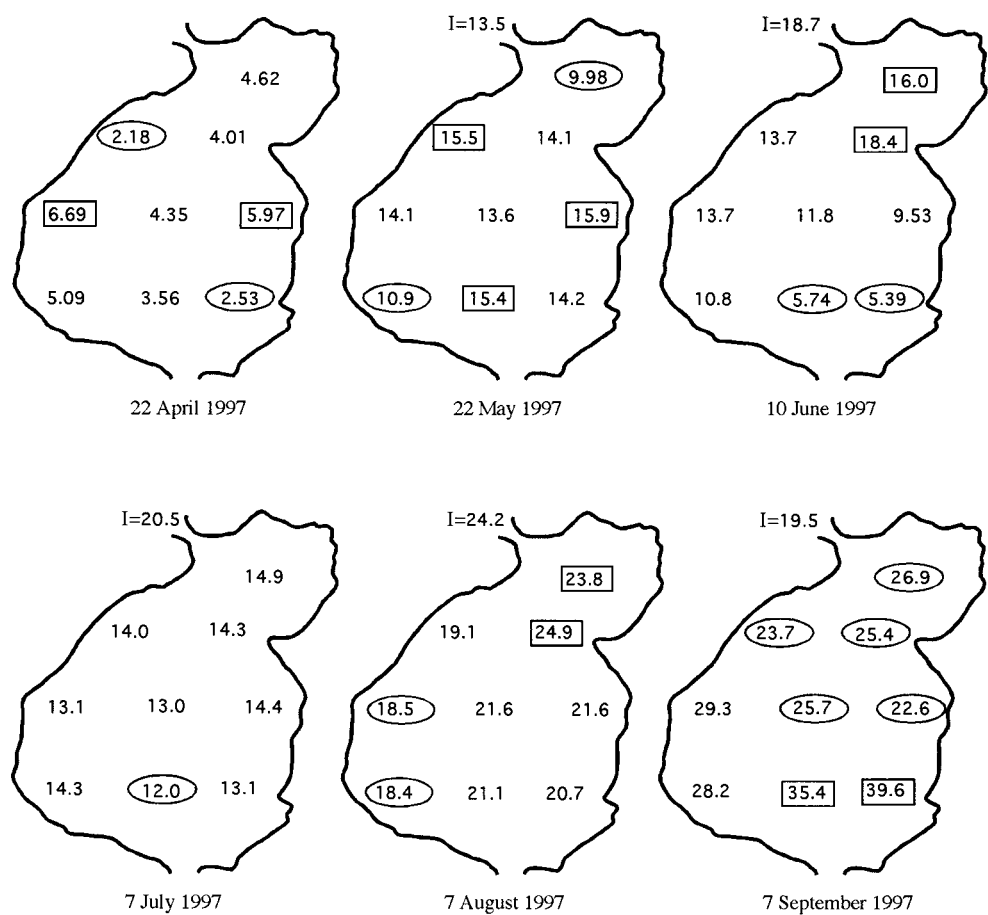
Fig. 4.   Individual station observations of arsenic (As)(III) (in nanomoles) for each month of this study. Rectangles denote values that were significantly above the lakewide average. Ovals mark values that are significantly below the lakewide average (95% confidence interval). The inflow concentration, denoted by I, was not available in April.

at the northern end, near the inflow (Fig. 4). Concentrations at the southern (outflow) end of the lake were much less than the lake mean. This roughly banded structure is consistent with the advection-dominated regime ($Pe > 1$; Table 2), for which mixing rates are too slow to erase spatial gradients along the direction of flow. Assuming a monotonic variation, the inflow concentration increases on average 0.27 nM d^{-1} between the May and June sampling dates. Given a residence time of 39 d and in the absence of significant transformation, this inflow variation would produce a north-to-

south decrease of 10.5 nM, consistent with our June observation. The heterogeneity in this month may also have arisen from in-lake transformation. That Da was >1 (Table 2) indicates that transformation rates were sufficient to contribute to As(III) heterogeneity, with oxidation decreasing the As(III) concentration as water entering from the north moved through the lake. In the absence of inflow variation, a typical oxidation rate of $k = 0.03$ d^{-1} would produce a decrease in As(III) of $kC_{mean}T_{res} = 13.6$ nM between the north and south ends of the lake, a value that was consistent with our ob-

Table 2.   Physical measurements and timescales.*

Date (1997)	$\overline{Q}$ (m³ s^{-1})	σ_Q (m³ s^{-1})	h (m)	T_{res} (d)	$\overline{W_{10}}$ (ms^{-1})	σ_W (ms^{-1})	T_{mix}(d) $D = 0.05$	0.1 m² s^{-1}	Pe $D = 0.05$	0.1 m^{-2} s^{-1}	Da
22 Apr	2.22	0.83	6	14	3.0	2.2	100	52	7.1	3.7	0.4
22 May	1.17	0.44	5	22	3.0	2.0	100	52	4.6	2.4	0.7
10 Jun	0.66	0.37	5	39	1.9	1.5	100	52	2.6	1.3	1.2
7 Jul	0.14	0.15	5	190	2.0	1.6	100	52	0.5	0.3	1.6–3
7 Aug	0.14	0.14	5	190	2.0	1.6	100	52	0.5	0.3	1.6–3
7 Sep	0.22	0.28	6	140	1.7	1.4	100	52	0.7	0.4	1.6–3

* Data for each date are based on averaged conditions over the preceding month.

servations (Fig. 4). To delineate the relative contributions of transformation and inflow variation, however, requires better temporal resolution of the inflow concentration as well as better estimates of k.

In contrast to spring, during the summer months the physical regime is diffusion dominated (i.e., net physical processes promoted homogeneity, and inflow variation is unlikely to produce significant patches). As $Da > 1$, heterogeneity in As(III) may still arise from local differences in net transformation rates. With $Pe < 1$ and $Da > 1$, the increasing value of As(III) HI between July and September is attributed to transformation. As both the residence time and mixing time are greater than the monthly sampling interval (Table 2), patches formed in one month may persist to the next, so that HI should increase from month to month, which would be consistent with the trend we observed. In contrast, the total As concentration became increasingly homogeneous over this period, which is consistent with the fact that total As heterogeneity is unaffected by transformation and that the physical processes that might contribute to total As heterogeneity are negligible (i.e., $Pe < 1$).

Conclusions

Chemical heterogeneity is a measurable and significant attribute of UML and probably of many similar small lakes. Its occurrence is consistent with simple scaling arguments based on observed physical processes and transformation rates. Both inflow variation and internal transformations appear at different times to be of sufficient magnitude to produce the observed chemical heterogeneity. Furthermore, because we did not base sampling times on major hydrological, meteorological, or biogeochemical driving events, it seems likely that greater degrees of heterogeneity than we observed may be common occurrences in lakes such as UML. For example, larger spatial variance is expected after storms, upwelling events, or buoyancy-/wind-driven exchange with bordering wetlands or in association with local enhancement or suppression of gross oxidation or reduction rates, which could create large variations in net As transformation. Further studies, conducted with higher spatial and temporal resolution, are needed to quantify specific mechanisms.

The observed magnitude and persistence of heterogeneity indicates that even within small lakes, a single sampling point cannot be used for lake-scale characterization. Rather, a sufficient number of distinct samples must be collected to quantify the spatial variance. Spatial variance may often exceed analytical variance and may thus represent the more significant component of uncertainty in estimating lake-scale inventories of water-quality parameters. During periods of high Pe, inflow variation may contribute significantly to spatial heterogeneity (e.g., as suggested for June 1997 in UML). Under these conditions, the sampling of inflow should have sufficient temporal resolution to resolve the dominant timescales of inflow variation. Unless the contribution of inflow variation can be quantified, reliable estimates of in-lake transformation rates cannot be made from spatial patterns alone. During periods of low Pe, when inflow variation contributes little to in-lake heterogeneity, observations of suf-

ficient spatial resolution to define patch scale may be used to estimate transformation rates following Eq. 4.

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