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Hydrologic Variability of Small, Northern Michigan Lakes Measured by the Addition of Tracers

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ABSTRACT

The hydraulic residence time (or flushing rate of water) is a key variable for any aquatic ecosystem and is used in many types of models and calculations. Rather than being measured directly, the hydraulic residence time is usually inferred from estimates of watershed size, precipitation, and water yield. Such estimates can be problematic in any environment but are especially so in environments in which flat or complex topography makes delineations of mapped watershed boundaries difficult to discern. We added lithium bromide, (LiBr) to three small seepage lakes in the flat topography of the Upper Peninsula of Michigan to provide an independent estimate of the water residence time. Water residence time [volume/(outflow + evaporation)] averaged 921 ± 381 (SD) days among lakes and years and ranged from 400 to 1661 days at the extremes. This variation was not clearly related to year-to-year variation in precipitation, which was relatively constant [0.26 ± 0.06 (SD) cm day (d)$^{-1}$]. The addition of the tracer (along with measurements of lake volume) enabled us to estimate, independent from other hydrologic information, the flow of water leaving the lakes in seepage plus surface outflow. This value, in conjunction with measurement of precipitation and evaporation, enabled us to calculate complete water budgets for these lakes. Among lakes and years, the groundwater input averaged 0.48 ± 0.36 cm d^{-1} and accounted for 57% ± 19% of total water input. This estimate was larger by 150% than that obtained by multiplying precipitation (minus estimated evapotranspiration) times a mapped value of the watershed areas. Our analysis enables us to calculate the relative significance of groundwater and precipitation for solutes such as phosphorus, hydrogen ion, and dissolved organic carbon.

Key words: hydraulic residence time; hydrologic variability; lakes; Michigan; tracers; watershed.

INTRODUCTION

An important variable for any aquatic ecosystem is the hydraulic residence time or flushing rate of water. The amount of time that water resides in a lake controls the amount of time available for critical biological and chemical reactions to occur. A good example of residence-time dependence is the relationship between the concentration of total phosphorus (TP) in the water and the input of TP from the watershed:

$$[P_m] = L_p/q_s[(1 + Z_m/q_s)^{0.5}] \quad (1)$$

where P_m is the average concentration of TP in the lake (µM), L_p is the loading rate of P to the lake per unit surface area [µmol P m^{-2} year (y)$^{-1}$], q_s is the annual load of water expressed per unit area of lake surface (m y^{-1}), and Z_m is the mean depth of the lake. The quotient Z_m/q_s is the water renewal time of the lake, equivalent to the flushing rate, ρ, used by Dillon and Rigler (1974) and others. Because chlorophyll *a* can be predicted from [P_m], this equation, or modifications of it, have been used extensively in

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eutrophication studies, but this equation is simply a special case of a large class of mixed reactor models (Chapra and Reckhow 1983). Although the various equations have different forms and units, they all require some measure of the input of water from the watershed.

The hydraulic residence time is difficult to measure directly and is usually inferred from other measurements. The individual components of the water balance of a lake are seldom measured with the same degree of certainty (Winter 1981). Further, one or more components are often estimated indirectly or determined as the difference between other measured components (Winter 1981). Where surface outflow or inflow are both directly measurable and known to be the dominant fluxes of water, the theoretical residence time is often expressed as the volume of the lake divided by the inflow or outflow rate (Chapra and Reckhow 1983). For internally draining lakes that lose no water to outflow or seepage, a similar approach can be used in which the volume is divided by the net evaporation rate, calculated from the mass balance of ^3H (Herczeg and Imboden 1988). A more common way to assess the water residence time is to estimate the yield of water from the watershed from precipitation and climate, possibly with refinements for geology, local hydrology, slope, shape, and land use, and use this as an estimate for the input of water (Ward and Elliot 1995). Less common are measurements of water input by using gauges on streams, networks of wells, or seepage meters (Malueg and others 1975; Schindler and others 1976; Likens 1985; Winter and others 1989; LaBaugh and others 1995). Given the resources needed to measure water inputs accurately, estimates of water yield to determine water input are appealing, yet not straightforward (Winter 1981; Ward and Elliot 1995). In relatively flat areas with a high density of lakes, for example, it is even difficult to estimate the size of the watershed from topographic maps. These difficulties result in high uncertainty associated with estimates of groundwater input to lakes (Wentz and others 1995). In some cases, it has been possible to use naturally occurring tracers, such as the $^{18}O/^{16}O$ ratio to estimate the groundwater input (Dincer 1966; Krabbenhoft and others 1990) and greatly improve the estimates for the water balance.

We have been working on a series of small seepage lakes that lie in a lake-dense region of flat topography in the Upper Peninsula of Michigan. We were particularly interested in the joint effects of nutrient loading (bottom-up) and fish manipulations (top–down) in structuring these lake ecosystems (Carpenter and Kitchell 1988; Pace and Cole 1994, 1996; Carpenter and others 1995; Pace and others 1998). Because the expected effects of nutrient loading depend on water residence time, we needed an estimate of it (Carpenter and others 1995). Water input to these lakes occurs from precipitation and groundwater, and water exits by both surface outflow and seepage (Carpenter and Kitchell 1993). The flat topography makes delineation of the watershed boundaries unclear and water yield difficult to estimate. To overcome these problems, we added small amounts of lithium bromide, (LiBr) to three experimentally manipulated basins and followed the dilution of this tracer for several years. Although purposeful hydrologic tracers such as Li have been used in flowing water for some time (Bencala and others 1990), this approach has not been attempted in many lakes (Bird and others 1995). Here we describe the results of such additions and simple methods to calculate water residence time.

METHODS

Study Site The lakes are part of the University of Notre Dame Ecological Research Center (UNDERC) and have had a long history of limnological investigation (Hasler and others 1951; Carpenter and Kitchell 1988, 1993). Located near Land O'Lakes, Wisconsin (89°32′W, 46°13′N), these lakes are situated in one of the most lake-rich districts of the United States (Marin and others 1990). The topography consists of flat to gently rolling terrain with extensive areas of bog or low-lying forest between the lakes (Figure 1). Lake level can vary year to year, because of variations in regional precipitation (Webster and others 1996).

We added LiBr to Peter Lake and to the East and West basins of Long Lake (Table 1). Long Lake was divided into three basins for manipulative experiments (East, Central, and West) by the construction of two impermeable curtains in 1992 (Figure 1) (Christensen and others 1996). Peter and Paul Lakes were divided from each other by the construction of an earthen dike in 1946 (Hasler and others 1951). Due to surface elevational difference, water drains from Paul into Peter through a culvert. All of the lakes are groundwater fed, with surface inflows rarely observed. Similarly, although the lakes have surface outlets, these rarely flow during the summer field season.

LiBr Additions and Sampling A concentrate of LiBr (54% LiBr by weight) was purchased from FMC Corporation (Gastonia, NC, USA). We diluted

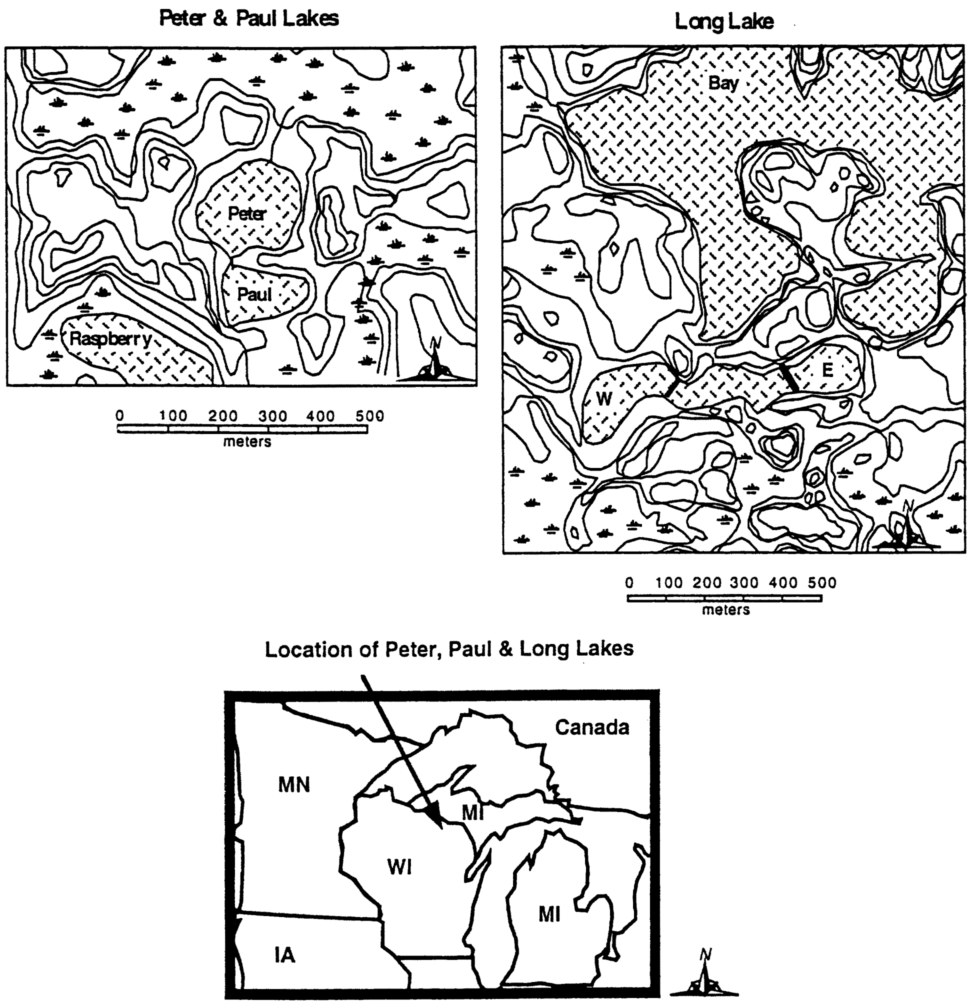

Figure 1. Location of Peter, Paul, and Long Lakes. The lakes are part of the University of Notre Dame Environmental Research Center located on the border of Wisconsin and the Upper Peninsula of Michigan (bottom panel). The three study lakes are on the Michigan side of the border. The map of the study site shows the location of the lakes (bottom panel) and the local topography around the lakes (top panels). Lakes are hatched and topography lines represent 3-m contour intervals. Long Lake consists of three basins separated by two curtains at the constrictions installed in 1991 (see the text). E and W, East Long basin and West Long basin.

Table 1. Characteristics of the Lakes and Schedule of the LiBr Additions

Basin	Lake Area (ha)	Watershed Area (Excluding Lake) (ha)	Mean Depth (m)	LiBr Additions 1992	LiBr Additions 1993	LiBr Additions 1994–96
Peter	2.67	7.97	5.70	None	Added	None
East Long	2.31	4.67	5.42	Added	Added	None
West Long	3.39	7.36	4.75	Added	Added	None

the concentrate into lake water and poured this solution through the propeller wash of a moving boat to enhance the mixing rate. At 1 day and at 1 week after the additions, we determined the spatial extent of the tracer in the surface water to assure that horizontal mixing had occurred, by sampling at 10 locations in two lakes. In 1992, we added LiBr to the East and West basins of Long Lake for a target concentration in the epilimnion of 15–20 µM; in 1993, we boosted the remaining LiBr by about 10 µM to restore an epilimnetic concentration of about 20 µM in the East and West basins of Long Lake and we added 20 µM to Peter Lake (Table 1).

From each basin, we took samples for Li^+ and Br^- in the surface water at weekly intervals. Additionally, we took samples at seven depths 5–8 times each year. Samples were taken by peristaltic pump (sample contacts no metal) into acid-washed polyethylene bottles that had been rinsed well [three times with tap water, once with deionized (DI) water, and twice with sample prior to filling]. Samples were filtered through Whatman GF/F filters to remove particles and were stored in acid-washed polypropylene bottles (rinsed as above), pending analysis. Br^- and Cl^- were measured on a Dionex model 500 ion chromatograph with AS4 A and AG4 A columns using the ASRS suppressor. Li^+ was measured by atomic emission spectroscopy at a wavelength of 670.8 nM on a Perkin-Elmer model 2380 atomic absorption/emission spectrophotometer. In both cases, certified standards were purchased from Alpha Chemicals. For Br^-, our limit of detection was 0.01 μM; for Li^+, it was 0.15 μM. We also sampled the diluted concentrate of LiBr that we added.

Estimates of the background concentrations of Li^+ and Br^- were obtained in several ways. Each basin was sampled several times prior to the addition of LiBr. Further, the surface water of a lake to which no LiBr was added (Paul Lake, Figure 1) was sampled at weekly intervals during the 1993 field season, and depth profiles were taken at the same schedule as the other lakes. Finally, during the first year of addition, the hypolimnetic concentrations of the basins that received LiBr into their surface waters provided an additional estimate of the background levels.

Sediment Sorption Experiment The use of LiBr as a tracer of water renewal rate depends on Li^+ and Br^- behaving as conservative ions (Bencala and others 1990). To examine the possibility for nonconservative behavior due to sorption, we added a series of LiBr concentrations to water and sediments of each basin. Approximately 600 g of wet, littoral sediment was collected from each lake, and 100 mL of DI water was added. LiBr was added at several concentrations to these and to a control consisting of DI water without sediments. The samples were shaken and then sampled 2 h after the addition.

Mapping and Climatological Data To delineate the watersheds of the lakes, we used US Geological Survey (USGS) 7 × 7-foot 1:24,000 topographic maps. High-quality hypsometric maps of the lakes were made in August 1993. To do these, several reference points on each lake were triangulated using a KVH Industries, Middletown, RI datascope flux-gate compass. Using these and midlake landmarks, a series of constant speed transects were run. Depth data were collected using the data stream from a discriminating digital sonar logged on a laptop computer. Data were collected at a rate of 1 observation per second. Thus, between 4000 and 8000 sets of depth and latitude and longitude coordinates were collected in each lake. The resulting maps differ only slightly from earlier maps made by depth soundings during ice cover (Carpenter and Kitchell 1993). Each lake is equipped with a permanent staff gauge that is monitored at weekly intervals. This enables us to calculate week-to-week changes in lake volume.

For all years except 1992, the first year of the study, we have daily precipitation at the UNDERC laboratory, within 2 km of the lakes. Additionally, we have data from National Oceanographic and Atmospheric Administration records from nearby meteorological stations (Minocqua, Eagle River, and Watersmeet). For 1992, we averaged arithmetically all of the available precipitation data. For subsequent years, we used the UNDERC values. The UNDERC values were well correlated ($r = 0.95$) with the averages of the other meteorological stations for the years of overlapping data. Evaporation off the surface of the lakes was estimated from the data in Woo and Winter (1990). To estimate regional values of evapotranspiration (ET), we used long-term (1902–85) discharge and precipitation data for the Wisconsin River and St. Croix River compiled by van der Leeden and others (1990).

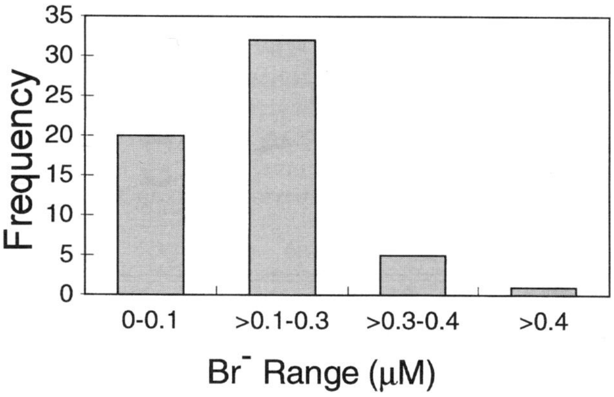

Figure 2. Frequency diagram of background concentration of Br^- for the University of Notre Dame Ecological Research Center lakes. Shown are the number of samples in each concentration class. Samples came from Peter Lake and the East and West basins of Long Lake prior to the addition of LiBr and from Paul Lake in 1993, to which no LiBr was added. For comparison, in the initial years of LiBr addition, concentrations were near 20 μM.

RESULTS

Background LiBr Prior to the addition of the tracer, concentrations of Li^+ and Br^- in the lakes were very low. Background Br^- concentrations averaged 0.13 ± 0.03 (standard deviation, SD) μM and background Li^+ averaged 0.21 ± 0.05 μM (Figure 2). The added tracer increased the initial concentrations by about 100-fold, enabling us to measure it easily, unconfounded by variations in natural background (Figure 3). Even in the final year of the experiment (1996), surface-water concentrations of both Li^+ and Br^- were more than 10-fold above these background levels.

LiBr Additions After each initial addition, and after the secondary additions in the East and West

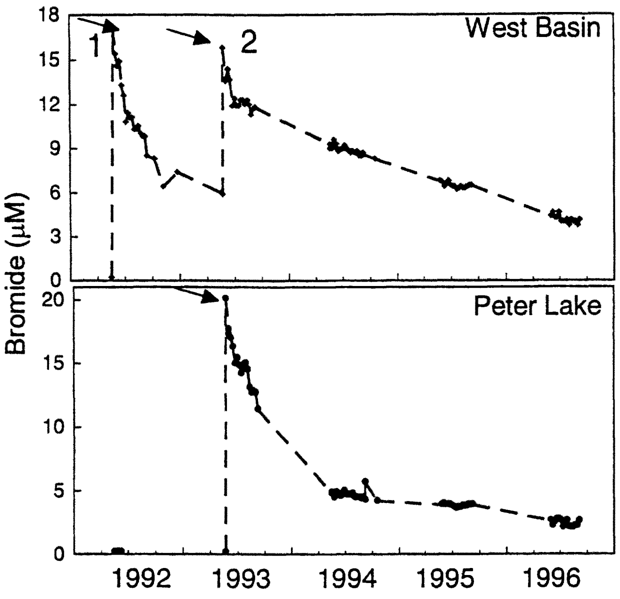

Figure 3. Concentrations of Br^- in West basin (top) and Peter Lake (bottom) over time. LiBr was added to West Long Lake in May of 1992 and again in May of 1993 (arrows 1 and 2). LiBr was added to Peter Lake only once in May of 1993 (see Table 1).

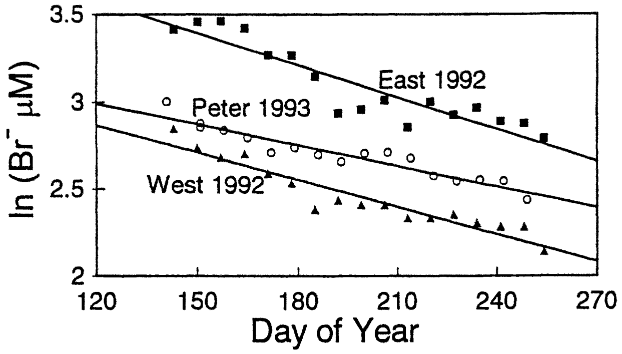

Figure 4. Exponential decline in the concentration of Br^- in the surface waters of Peter Lake (open circles), East Long Lake (solid squares), and West Long Lake (solid triangles) during the first season of addition for each lake. The points are weekly measurements (note the natural log scale), and the lines are linear regressions.

basins of Long Lake, Li^+ and Br^- initial concentrations were near 15–20 µM in the different basins. These concentrations declined monotonically in the surface waters over time (Figure 3). During the time of initial additions (1992 in East and West and 1993 in Peter; Table 1), the declines in Li^+ and Br^- concentrations fit a negative exponential function (Figure 4). The slopes of these curves represent the loss rates of Li^+ and Br^- concentrations from the surface waters due to both dilution with incoming water and to deepening of the hypolimnion. After the first autumnal mixis, the situation is more complicated since the hypolimnia also contained LiBr (below).

Vertical Mixing In the vertical dimension, the added tracer was mixed evenly into the upper mixed layer (Figure 5). As the thermocline deepened, the region labeled by Li^+ and Br^- expanded and after autumnal mixis the lakes were uniformly labeled with the tracers. There was no evidence of transport of LiBr across the thermocline. We saw no detectable increases in Li^+ or Br^- in hypolimnetic water below the thermocline during the initial LiBr additions (Figure 5).

Horizontal Mixing The added tracer was very rapidly mixed within the epilimnion of the lakes. At 24 h after the addition of the LiBr, the concentrations of both Li^+ and Br^- did not differ significantly across locations of the East or West basins. The coefficients of variation of these spatial measurements of Br^- and Li^+ were 2.9% and 4.6% in East and 2.5% and 2.6% in West, respectively, for 10 locations in each basin.

Sediment Sorption We saw no evidence that added Br^- was removed from the water column even after vigorous interaction with the sediment in our short-term experiments. A plot of the measured Br^- concentration against the concentration added shows no removal of the added Br^- (Figure 6). The same plot for Li^+ suggests the possibility that some Li^+ may have sorbed at the highest concentration tested. As this concentration (60 µM) was more than twofold above what we added to any of the basins, it is likely that Li^+ sorption did not occur in the lakes. This conclusion is strengthened by a plot of Li^+ versus Br^- from all of the data for all of the lakes to which LiBr was added (Figure 7). The relationship between the concentration of Li^+ and Br^- is nearly perfect ($r^2 = 0.98$). The ratio of Li^+ to Br^- is above 1.0 (slope = 1.14 ± 0.01), which is consistent with our analysis of the added LiBr solution. Cl^- accounts for about 10% of the total anion content in the original diluted concentrate. The strong correlation between Li^+ and Br^- in the lakes suggests either that both ions were conservative or that each was sorbed to the same degree. Equal sorption of Li^+ and Br^- is neither likely nor is it consistent with our sorption experiments. We express our results below in terms of the Br^- mass or concentration; almost identical results would be obtained by using Li^+ as the basis of the calculations.

Calculation of Water Residence Times Because of the low background concentrations, we can use the concentrations of added Li^+ and Br^- to estimate parameters related to water renewal rate. We need to distinguish, however, between the residence time

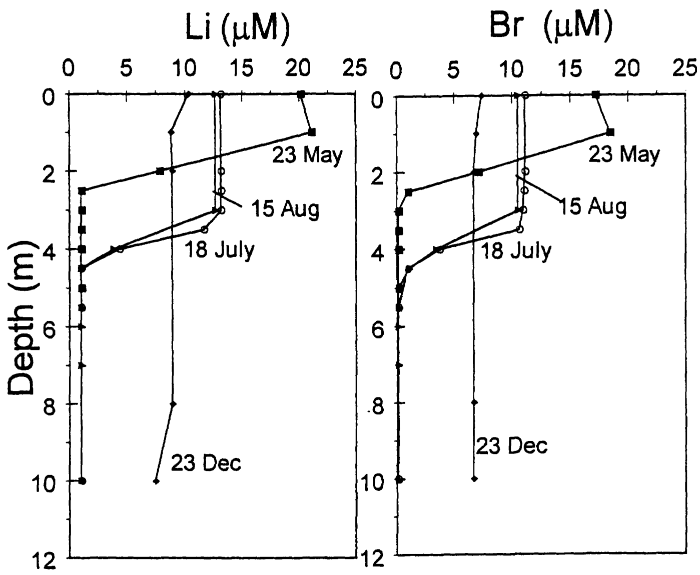

Figure 5. Depth profiles of the concentrations of Li^+ and Br^- in West Long Lake during 1992 (the first year of LiBr addition). Each line represents a profile taken on a different date (solid squares, 23 May; open circles, 18 July; solid triangles is August; solid diamonds, 23 December). Autumnal mixing occurred in October.

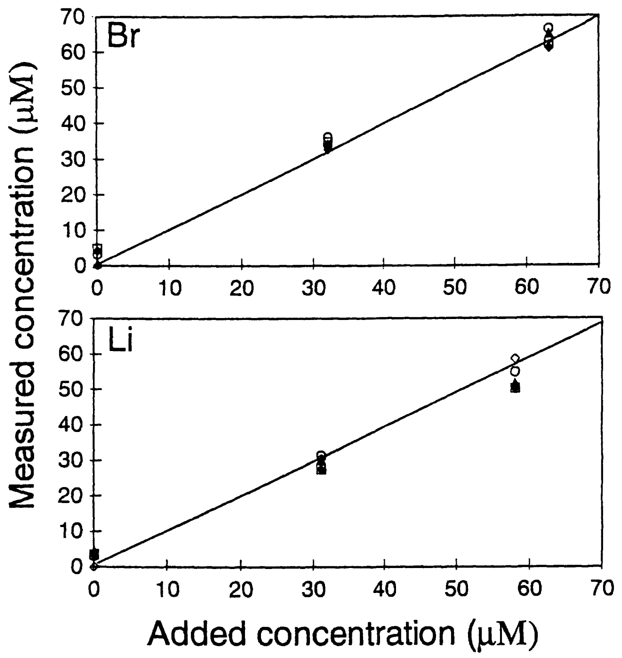

Figure 6. Results of a sediment sorption experiment for Br^- (top) and Li^+ (bottom). Concentrations of LiBr were incubated with water and sediments (see the text) from four of the University of Notre Dame Ecological Research Center lake basins. Plotted are the measured concentrations of Li^+ and Br^- (symbols) and the concentration that should have been obtained had no sorption occurred (added concentration). Paul Lake, solid triangles; East Basin, solid diamonds; West Basin, open squares; Peter Lake, open diamonds.

of a solute (for example, LiBr), which will depend on the depth distribution of the solute, and that of the water, which does not. Also, water can be lost by evaporation, decreasing its residence time, but a enters and exits these lakes primarily in littoral solute can not. If we assume that seepage water sediments (McBride and Pfannkuch 1975; Lee 1977; Shaw and others 1990), then when only the epilimnion is labeled with LiBr, a plot of the natural log of mass of Li^+ or Br^- versus time will give both the dilution rate of the solute and the input rate of the diluting water, ignoring, for now, the small concentrations of Li^+ and Br^- in the incoming water. After the first autumnal mixing, the incoming water dilutes the tracer in the epilimnion but not in the hypolimnion. By the following spring, the concentration of the tracer is lower in the epilimnion than in the hypolimnion. Thus, for the subsequent years after the initial addition, we need to consider two points. First, the residence time of the solute is now longer than the residence time of the water because some of the solute resides in the hypolimnion, where new water input by seepage and rainfall is negligible. Also, there is a significant input of the tracer into the epilimnion as the thermocline deepens that needs to be accounted for in a mass balance of the tracer in the epilimnion. Thus, although the slope of a simple dilution plot [ln (Br mass) versus time] will be the inverse of the residence time during the first year of addition; this approach will not work in subsequent years.

To compute the water residence times from the LiBr data, we used a simple mass balance, which enables us to solve for amount of water flowing out of the lake in seepage plus surface flow. We assume that LiBr can leave the lake only in flowing (seepage plus outflow) water and that LiBr exits the lake at the mean epilimnetic concentration for the time period of interest. Further, since we know that the

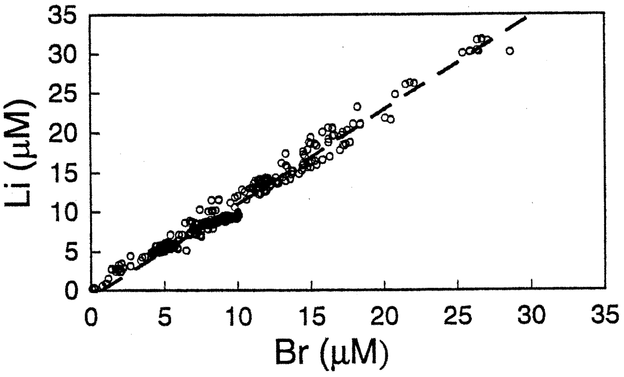

Figure 7. Measured concentrations of Li^+ versus Br^- from the three basins to which LiBr was added. Shown are all the measurements for the weekly samples in the surface waters of Peter Lake and East and West Long Lakes for which Li^+ and Br^- were both measured. The dashed line is the regression: $Li^+ = 1.14 \times Br^- - 0.59$; $r^2 = 0.98, n = 511$.

concentration of Br^- in the lake is much higher than the concentrations in incoming groundwater or precipitation, we can ignore those inputs; this assumption gives us a very slight underestimate of the true outflow volume.

The mass of bromide (moles per lake) in the lake (Br_{mass}) is the sum of the concentrations of Br^- in each layer ($[Br^-]_i$) times the volume in that layer ($volume_i$):

$$Br_{mass} = \Sigma\ volume_i \times [Br_i] \qquad (2)$$

The change in Br_{mass} over time is the Br^- mass loss [mol Br^- day $(d)^{-1}$]. $[Br^-]_i$ is measured directly from the vertical profiles taken in the lake. $Volume_i$ is estimated from hypsographic curves for each basin, corrected for changes in lake level (from the staff gauges). We can then estimate the volume of water that left the lake in seepage plus surface outflow:

$$outflow = Br\ mass\ loss/[Br_{epi}] \qquad (3)$$

where outflow ($m^3\ d^{-1}$) is the volume of water exiting the lake in seepage plus outflowing stream water and $[Br_{epi}]$ is the mean concentration of Br^- in the epilimnion during the period over which the mass loss is computed. We do this in two ways: for each individual period between dates on which profiles were taken, and for the entire season (start to finish). Finally, for the initial years of addition (and for the year in which we boosted the epilimnetic concentration with a second addition in East and West basins of Long Lake; Table 1), we computed the solute residence time by a regression of the natural log of the mass of Br^- in each lake against time. The results are summarized in Figure 8A. These estimates of residence time are based on a totally nonvolatile solute that moves with water. Among lakes and years, the average residence time was 1624 ± 1124 days. Much of this variance was related to very long calculated residence times in 1996 that could be the result of low tracer concentrations. Excluding 1996, the residence time was 1239 ± 819 days. The residence time was not correlated to precipitation ($P > 0.1$, Pearson correlation) whether or not we included 1996.

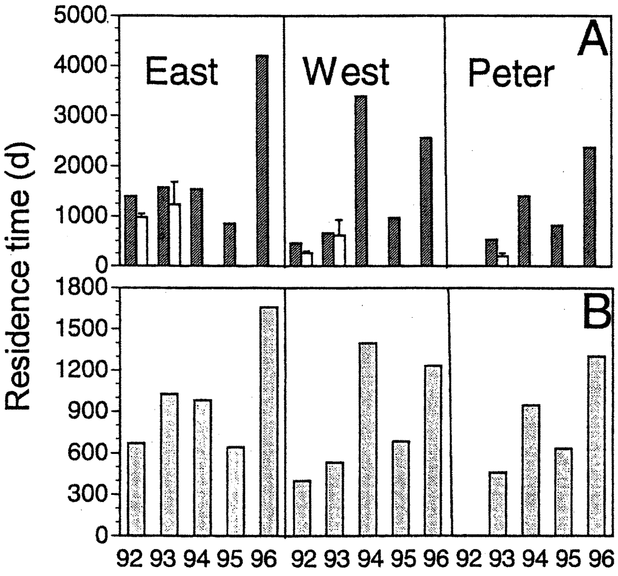

Figure 8. Estimates of water residence times in the three basins based on the additions of LiBr. **A** Residence time is calculated as lake volume/outflow and is the residence time for a nonvolatile solute. For the cross-hatched bars, we used loss of Br^- mass to compute water outflow (see the text). The open bars are derived from a plot of the natural log of Br^- versus time in the initial years and booster year (1993 in East and West Long Lakes) when most of the Br^- resided in the epilimnion. The error bars are standard errors of the regression slopes. **B** Residence time is calculated for water: volume/(outflow + evaporation). Note change in scale in y-axis. In both A and B, the residence time would be faster if the volume of the epilimnion were used instead of the volume of the lake.

Because of evaporation, the residence time for water is actually faster than that just calculated. We provide estimates of the residence time, including the evaporative term (see below), in Figure 8B. Averaged among lakes and years, the water residence time was 921 ± 381 days for all years and 864 ± 329 days, excluding 1996.

Calculation of Water Budgets The full water balance for a lake is shown in Eq. 4:

$$GW + P + SF = O + E + \Delta S \qquad (4)$$

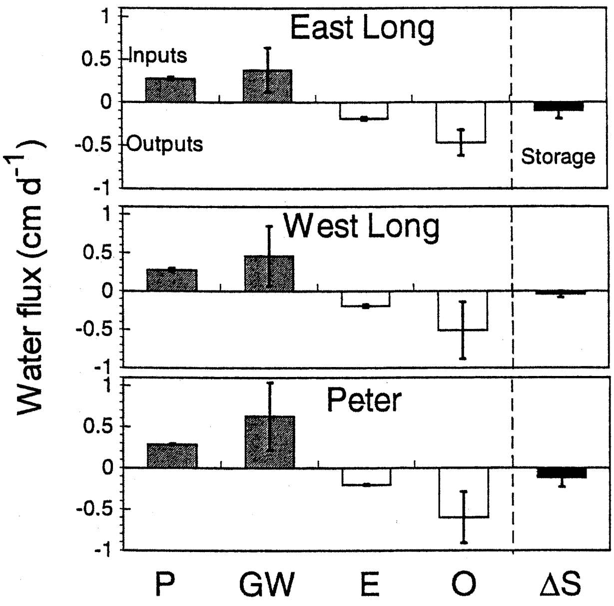

Figure 9. Average water budgets for the three lakes, based on the addition of LiBr. Shown are mean fluxes for the period of record (1992–96 in East and West Long Lakes and 1993–96 in Peter Lake) along with standard deviations representing interannual variation. P, precipitation input; GW, groundwater input; E, evaporation; O, outflowing water in seepage plus surface flow; ΔS, the change in water storage (volume) in the lake. Positive values are inputs and negative values are outputs. For ΔS, a loss in volume is plotted here as a negative value.

where GW is the groundwater input, P is the precipitation input, SF is surface-water input, O is outflow in seepage plus surface flow, E is evaporation, and ΔS is the change in volume. We used the Br^- tracer (above) to estimate O. Because SF is essentially zero in our system, we have one true unknown: GW. E is estimable, albeit crudely. Based on the maps for this region in the volume by Woo and Winter (1990), average annual E is 0.15 cm d^{-1}; this value is 68% of annual precipitation. Using this approximation for E relative to P, we can calculate GW. To minimize uncertainty, we did this only for the entire sampling season (start to finish) for each lake. These results are summarized in Figure 9, and a specific example given below. Rearranging Eq. 4 and putting in actual values (cm d^{-1}), the water budget for West Long Lake in 1993 would be

$$GW = O + E + \Delta S - P - SF$$

$$GW = 0.71 + 0.18 + 0.1 - 0.27 - 0 = 0.72 \text{ cm d}^{-1}$$

In all cases but one (Peter, 1994), each lake lost volume over the summer season. These losses were variable, but much smaller than the losses due to the outflowing water and averaged 15.9% ± 13.2% (SD) of outflow volume among lakes and years. Estimated evaporation was nearly half as large as outflow (48.6% ± 34.3% averaged among lakes and years). Averaged among lakes and years, the calculated GW input was 0.48 ± 0.36 cm d^{-1}. Of the total water input to the lakes, direct precipitation in the lake's surface accounted for 45.4% ± 21.4%.

How well would a topographic map based estimate of water input agree with our tracer-based measurements? Using the USGS maps (see Methods), and our on-site measurements of precipitation, we can calculate the water input to these lakes with the additional information of water yield per unit precipitation. Long-term (1902–85) annual water yield data for the Wisconsin and St. Croix Rivers are 44% and 40% of annual precipitation (P), respectively (van der Leeden and others 1990). Thus, average annual ET is about 56%–60% of P. At an ET of 60%, the LiBr-based estimate was 1.5 ± 0.1 times greater than the map-based estimate across lakes and years (Figure 10). Since ET is the least certain number in this estimate, we recalculated water input, allowing ET to vary. To get reasonable agreement between the tracer and map estimates, ET would have to be quite low, only 40% of annual precipitation (Figure 10).

DISCUSSION

The use of the LiBr tracer takes some uncertainty out of estimating some components of the water balances of these small lakes. In our application, we were able to calculate independently the outflow of water in seepage plus surface flow by means of the tracer. With outflow known, along with measurements of precipitation and changes in lake volume and regional estimates of evaporation, the input of groundwater could be calculated by difference. In the absence of sophisticated mapping and hydrologic measurements, one does not know how well a topographic map represents the actual watershed, nor would one have a good estimate of ET. Using a regional value for ET, and existing USGS topographic maps to estimate the watershed size, the map-based calculated input of groundwater was considerably lower than that based on the LiBr additions. The possible reasons for this discrepancy are numerous. It is conceivable that the local water yield is much higher than the regional average and that locally ET is in fact close to 40% of P. Further, in the relatively flat topography of this area, it is difficult to visualize watershed divides by using available maps (Figure 1); if the watersheds of the lakes were consistently larger than we mapped them, the discrepancy could be eliminated. Also, in

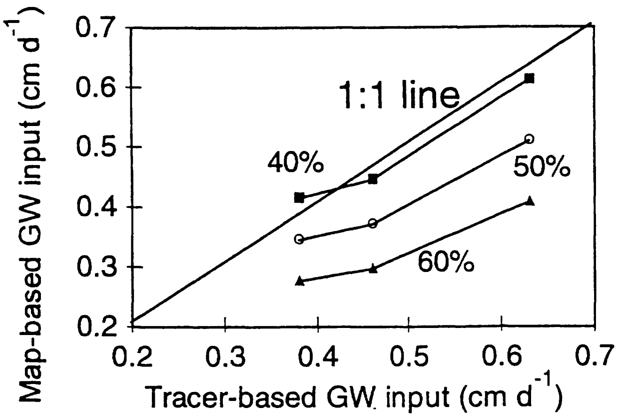

Figure 10. Relationship between two independent estimates of average groundwater (GW) loading to the three University of Notre Dame Ecological Research Center lakes studied. The *x*-axis shows GW inputs based on the additions of LiBr (tracer based), and the *y*-axis shows GW inputs based on multiplying an estimate of water yield times the area of the terrestrial watershed (map based). The points show map-based calculations for different assumptions about evapotranspiration (filled triangles, ET = 60% of precipitation; open circles, ET = 50% of precipitation; filled squares, ET = 40% of precipitation; see the text). For each assumed value of ET, we have plotted the calculated water input for each of the three basins against the average of the tracer-based estimate for the years of record. Points falling near the 1:1 line would indicate perfect agreement between the two approaches; this agreement would occur if ET were near 40% of P. For North Michigan ET, regional ET is near 60% of P or 0.15 cm day^{-1}. At ET = 60% of P, the map-based approach substantially underestimates GW input based on the tracer.

this terrain, the groundwater elevations may not consistently conform to the variations in land-surface height (Krabbenhoft and Webster 1995; Wentz and others 1995). In addition, we have no estimates for either changes in water storage in the watersheds or redistribution of snow across watershed boundaries. Finally, changes in lake level of nearby lakes by the intermittent activity of beavers could potentially alter the hydrology. For example, a rise of only a few tenths of a meter in nearby Bay Lake could cause this very large lake to flow into West Long rather than to drain it. Such changes may be responsible for some of the year-to-year variance we see in residence time that is not related to precipitation. The use of tracer additions offers a way to estimate water residence time that is largely independent of a knowledge of the size of the watershed, water yield, or details in the local hydrology.

The UNDERC lakes have relatively small watersheds in comparison to lake areas, which leads to relatively long residence times. A consequence of the small terrestrial watershed area is that direct precipitation on the lake's surface can be an important input of water. Precipitation could therefore be a significant input of materials that are more concentrated in rainwater than in lake water (H^+ or NO_3^{-1} for example). Christensen and others (1996), using peizometers, measured pH values in incoming porewater to East Long Lake and West Long Lake of 6.3–6.5. Regional pH values of rain are available from the National Acid Deposition Program site at Trout Lake, approximately 25 km from the study lakes. The mean pH of weekly samples for 1994 was 4.7 or 4.8, by field-based and laboratory-based measurements, respectively. The loading of H^+ to these lakes, then, is about 20 times greater by precipitation (approximately 4.3×10^{-5} mol m^{-2} d^{-1}) than by groundwater (about 2.2×10^{-6} mol m^{-2} d^{-1}).

Averaged among lakes and years, the groundwater input is 0.48 ± 0.36 cm d^{-1}. Although this is not a very rapid rate of water renewal, this input of groundwater can be quite significant for some materials. Vezina and Pace (1994), on the basis of an inverse modeling analysis, concluded that about 150–200 mg C m^{-2} d^{-1} of allochthonous dissolved organic carbon (DOC) input was required to support metabolism for the lakes in which the ratio of primary production to respiration was less than 1. Using our mean estimate for the input of groundwater and the mean DOC concentration in the porewater surrounding UNDERC lakes (Christensen and others 1996), we estimate that about 50–100 mg C m^{-2} d^{-1} of allochthonous DOC enters these lakes during May through September, an estimate not far from that of Vezina and Pace (1994).

Groundwater may also be a significant source of P to these lakes. Prior to fertilization, and in the unfertilized basins, the sedimentation of P into the hypolimnion, based on sediment traps, ranged between 1 and 2 mg P m^{-2} d^{-1} (Carpenter and others 1992a,b; Schindler and others 1993). The P output from the epilimnion must be supported by the inputs to the epilimnion plus changes in the TP mass in the epilimnion (Caraco and others 1992). In addition to fertilization, the possible inputs include groundwater, wet and dry deposition from the atmosphere, internal loading from epilimnetic sediments, and P loading from the hypolimnion. Our tracer experiment shows clearly that the hypolimnetic term is negligible given the lack of cross-thermocline transport and the relatively small increases in TP in the upper part of the hypolimnion (Cole and Pace 1995). The input of P in precipitation and atmospheric deposition is not known directly for UNDERC but can be crudely estimated from other data. Typical concentrations of particle-free P in rainfall are on the order of 0.1 µM L^{-1} (Likens 1985). For the UNDERC basins, this translates into a loading input of only 0.007 mg P m^{-2} d^{-1}. Cole and others (1990) estimated atmospheric P inputs to Mirror Lake to be about 0.4 mg P m^{-2} d^{-1}; this input could be larger in the UNDERC basins, which are considerably smaller than Mirror Lake, since P deposition tends to decrease with increasing distance from the shoreline (Cole and others 1990). Thus, prior to fertilization, about 40% of our lower estimates of P sedimentation could be supported by atmospheric deposition. If the remaining 60% were supported entirely by groundwater inputs, the concentration of TP in inflowing groundwater would have to be about 5 µM P. Hooper and Morris (1982) measured P concentrations in the water of the *Sphagnum* mat surrounding a small basin (North Gate Bog) on the UNDERC property, about 2 km from our study lakes. The P concentration increased with depth into the mat and with increasing distance away from the open water. Even in the surface water of the mat at a distance of only 1 m from the open water, they obtained concentrations of 3–20 µM, which is sufficient to balance the P output.

Useful hydrologic information can be obtained by the addition of soluble tracers such as LiBr (Bencala and others 1990). The addition of LiBr in standing water, however, should be used with caution, since organisms may be bathed in it for appreciable periods of time. Both Li^+ and Br^- can be toxic to some organisms. Although it is easy to add and detect both Li^+ and Br^- at levels far below those causing acute toxicity, the levels that may cause chronic problems are not well characterized and are somewhat controversial. Many researchers have considered Li^+ to be nontoxic at levels well above 1 mg L^{-1} (143 µM). It has been recently argued that Li^+ concentrations as low as 150–500 µg L^{-1} (21–71 µM) could, over time, affect the feeding behavior of freshwater snails and the survival and reproduction of fish (Stewart and Kzsos 1996). Although there is also evidence that even higher levels of Li^+ are not toxic (Tate and others 1996), the possibility of toxicity at these low levels is worth considering. Our maximum concentrations approached these new lower levels for toxicity (15–18 µM), but were sustained for only a few days following the initial additions (Figure 3). Flury and Papritz (1995) reviewed the literature on both acute and chronic toxicity to Br^- by a wide range of organisms. The lowest concentration they report as having any measured adverse affect on any organism was 0.023 g L^{-1} (291 µM) in a 3-week exposure of *Daphnia magna*; this concentration is about 15 times higher than the highest concentration we achieved in our additions. Based on the review, Flury and Papritz (1995) suggest that maintaining concentrations below 1 mg L^{-1} (12 µM) should avoid toxicity problems. In this case, we exceeded this target concentration for 2–3 weeks following the initial additions. We have no direct evidence of a toxic effect of LiBr additions in our system. However, until the concentrations of Li^+ and Br^- that may damage organisms are known with more certainty, we urge caution in the use of this tracer in lakes.

The use of deliberate tracers offers an approach to the estimation of hydraulic flushing rates that is free from many of the assumptions required in conventional hydrologic approaches. Further, the tracer approach can be used in cases where hydrologic information on the watershed may be difficult or expensive to obtain. It is not a pariacea, however, and its application is certainly limited to small systems.

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