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Stable isotope estimates of evaporation : inflow and water residence time for lakes across the United States as a tool for national lake water quality assessments

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Abstract

We used water δ^2H and $\delta^{18}O$ from ca. 1000 lakes sampled in the 2007 U.S. Environmental Protection Agency's National Lakes Assessment (NLA) to assess two hydrological variables—evaporation as a percentage of inflow ($E:I$) and water residence time (τ) for summer 2007. Using a population survey design, sampled lakes were distributed across the conterminous U.S., and results were scaled to the inference population (~50,000 U.S. lakes). These hydrologic variables were related to lake nutrients and biological condition to illustrate their usefulness in national water quality monitoring efforts. For 50% of lakes, evaporation was < 25% of inflow, with values ranging up to 113% during the 2007 summer. Residence time was < 0.52 yr for half of the lakes and < 1.12 yr for 75% of lakes. Categorizing lakes by flow regime, 66.1% of lakes were flow-though lakes (60% or more of the water flows through the lake, $E:I < 0.4$), 33.6% were restricted-basin lakes (40% or more of the lake inflow evaporates, $0.4 < E:I < 1$), and < 0.3% were closed basin (all water entering the lake leaves through evaporation, $E:I > 1$). While climate patterns drove some of the spatial patterns of $E:I$ and τ, variation in lake depth and watershed size (influencing precipitation volume) were also significant drivers. Lake hydrochemistry was strongly correlated to $E:I$ and more weakly related to τ. Lakes in poor biological condition (based on a predictive model of planktonic taxa) were significantly more evaporated than lakes in good biological condition.

The importance of lentic freshwater ecosystems in global-scale biogeochemical and hydrologic cycling has become increasingly apparent (Downing et al. 2006; Cole et al. 2007; Tranvik et al. 2009). Globally, lakes have been estimated to number > 64 million and cover > 3.8 million km^2 in area (Downing et al. 2006; McDonald et al. 2012). The role of lakes in these cycles has changed with human activities and is predicted to continue to change with climate change and further human activity. However, the data needed to describe the current status of lakes at this scale (continent or larger) are limited. One source of detailed lake information at the national scale comes from the U.S. Environmental Protection Agency's (U.S. EPA's) National Lakes Assessments (NLAs), which began in 2007 with plans to repeat the lake assessment every 5 yr.

During the 2007 NLA assessment, a wide variety of biological, recreational, chemical, and physical indicators were measured at > 1000 lakes across the U.S.A. and were used to evaluate the condition of the nation's lakes (U.S. EPA 2009). Using a probabilistic-based survey design, NLA results were scaled to represent the entire inference population of nearly 50,000 lakes (Olsen et al. 2009; Peck et al. 2013). While the information collected was extensive for water quality and biological diversity, hydrological indicators were initially limited to lake area and depth, basin area, and annual precipitation and other climate data. U.S. EPA defines lake ecological condition in terms of biological indicators; however, U.S. EPA is also interested in understanding stressors and causes of impairment such as excess nutrients, and including more detailed hydrological indicators in the national survey could help in this latter goal. The water quality and biological condition of lakes depend not only on local land use and disturbance to the lake and shores, but also on lake hydrological processes that link the surrounding landscape and climate to the lake (Fraterrigo and Downing 2008). Hydrological characteristics such as residence time and the proportion of water flow-through in a lake compared with evaporation have been linked to chemical stressors (Pham et al. 2008; Romo et al. 2013). One way to improve the NLA and our understanding of lentic systems at the continental scale would be to include more detailed measures of lake hydrological characteristics in national surveys.

Many of the biogeochemical functions that affect stressors and lake biology are strongly affected by lake hydrological characteristics (Tranvik et al. 2009). For example, evaporative concentration may increase the concentration of conservative ions, sometimes with dramatic effects on salinity (Anderson et al. 2001), and is generally associated with higher nutrient concentrations (Wolfe et al. 2007; Sokal et al. 2008). Longer residence times increase the cycling and potential retention of biologically active ions, including nutrients like phosphorus (Brett and Benjamin 2008; Koiv et al. 2011) and nitrogen (Kaste et al. 2003; Harrison et al. 2009). Longer residence times may also increase the sedimentation rates of toxic metals, reducing the concentrations of total mercury (Selvendiran et al. 2009) and heavy metals (Rippey et al.

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2004). The effects that hydrologic functions may have on potential stressors to biological assemblages underline the importance of assessing them in regional and national lake assessments. This importance will likely increase in the future as climate change affects rates of lake evaporation and hydraulic transit time (Malmaeus et al. 2006). Yet, direct measurements of many hydrologic processes cannot be conducted in a spatially extensive survey, where sites are randomly distributed and therefore often remote and where data collection is constrained by the number of measurements that can be conducted in a single day.

One approach that has been useful for assessing hydrological processes in lakes from broad-scale lake surveys was to measure the lake water $\delta^{18}O$ and $\delta^{2}H$ (Gibson and Edwards 2002; Gibson et al. 2002; Wolfe et al. 2007). The theory for estimating evaporation : inflow ($E:I$) and lake water residence time from stable isotopes has been well documented and refined over time (Gat 1995; Gibson et al. 2002; Gat 2010). The theory is based on isotopic mass balance and a detailed knowledge of isotopic fractionation during evaporation of lake water. If the isotopic value of water flowing into a lake is known (average isotopic value of surface water, groundwater, and direct precipitation), then the proportion of water that is evaporated from the lake can be estimated from the evaporative increase in $\delta^{18}O$ and $\delta^{2}H$ values of the lake water. Most studies where this isotopic approach has been used involve relatively few lakes with detailed sampling over time (Froehlich 2000; Gibson et al. 2002; Stets et al. 2010). Using water isotopes, Pham et al. (2008) determined how solute concentrations within lakes were related to lake evaporation and land use activities. Gibson and Reid (2010) illustrated how the lake isotope models could determine annual changes in the proportion of water entering a lake that leaves through evaporation ($E:I$) and further separate water loss mechanisms between the lake and the watershed. The isotopic method for determining basic lake hydrological characteristics is a practical alternative to classical hydrological monitoring for understanding water balance effects on water quality and biological condition of lakes where detailed lake hydrological data are not available (Gibson et al. 2002; Wolfe et al. 2007).

One potential challenge in using the water isotope approach for estimating lake hydrological parameters in an extensive survey such as the NLA is that only one water sample was collected during the summer, with 10% of lakes being sampled twice. The steady state models for estimating $E:I$ and residence time assume a constant and well-mixed volume of water, both of which are not accurate for many lakes. However, the steady-state model predictions provide estimates of $E:I$ and residence time that are representative of conditions at the time of sample collection, even though these conditions are dynamic and will change seasonally. The water isotope signal within a lake represents an integrated signal of lake water evaporation over the residence time of water within the lake and thus is more reflective of the average lake hydrologic condition with longer residence time (Gat 1995). Henderson and Shuman (2010) surveyed 100 lakes in the U.S. western mountains and found that lake isotopic values reflected weighted annual precipitation values compared with rivers, which were more influenced by isotopic seasonality in precipitation. Additionally, extensive surveys such as the NLA are not trying to predict the condition of any particular lake but are assessing the distribution of conditions across the continent for the assessment period: the summer of 2007. In the case of the NLA, a statistical survey design was utilized so that inferences across the population of lakes in the U.S. (e.g., the proportion of lakes with residence times > 1 yr during the assessment period) could be made with known confidence from sampling on a single day (Peck et al. 2013). Thus, point measurements for dynamic parameters such as lake nutrients and hydrological characteristics are reflective of a broad range of conditions that exist during the sampling period but are not meant to characterize any particular lake. Some broader scale regional lake studies have successfully estimated hydrological parameters from water isotopes based on single samples from lakes to assess the regional status of lakes (Gibson and Edwards 2002; Wolfe et al. 2007). Using the single isotopic sample approach, Gibson and Edwards (2002) were able to describe distinct hydroclimatic regimes of lakes adequately from three distinct biomes in northern Canada: tundra, boreal forest, and the ecotone between the two. Lakes within the boreal forest evaporated significantly greater proportions of the lake inflow compared with lakes in the arctic tundra. Wolfe et al. (2007) used $E:I$ estimates from single samples obtained from a survey of 57 lakes in northern Alberta to classify lakes into drainage categories and found a strong relationship between these categories and lake chemistry. Using this approach of assessing hydrological status using an isotope mass balance model and the hydrogen and oxygen isotopic composition of lake water determined on a single sample is well-suited to the logistical constraints of the NLA program and can provide information about the hydrological characteristics of lakes that are contemporaneous with the biological, chemical, and physical indicators collected during the survey.

Here, we use lake water evaporation theory for water isotopic ratios to predict $E:I$ and residence time (τ) during the 2007 summer assessment period for 1000+ lakes distributed across the contiguous U.S., and extrapolate those results to predict the distribution for the entire inference population of lakes (nearly 50,000 lakes) on the basis of an NLA statistically weighted survey design (Peck et al. 2013). The 2007 NLA survey represents the largest spatially extensive survey of lakes in the U.S. and the only lake survey to have a statistically based design for extrapolating the results to assess condition of lakes at the continental scale. Our goal was to assess the potential for isotopic analysis conducted on one water sample from each lake to be used to generate hydrological data at the continental scale and to provide hydrologic insights to lake water quality and biological condition status.

Methods

National Lakes Assessment—In the summer of 2007, the U.S. EPA conducted its first NLA as part of the National Aquatic Resource Surveys (U.S. EPA 2009). A total of

1028 lakes across the contiguous U.S. were selected using a probability-based survey design, with 10% being randomly selected for a second sampling later in the summer (Peck et al. 2013). The survey design means that the results from the 1028 lakes can be extrapolated to the entire inference population of lakes found within the U.S. that fit the following criteria. The inference population included both natural and man-made lakes if they were > 0.04 km^2 in area, at least 1 m deep, and with a minimum of 0.001 km^2 of open water. Each lake was designated as man-made or natural on the basis of visual examination of maps; all impounded lakes were designated as man-made. The survey excluded the Great Lakes, the Great Salt Lake, commercial treatment ponds, disposal ponds, brackish lakes, and ephemeral lakes. Using the National Hydrography Dataset, Peck et al. (2013) estimated that 68,223 lakes in the contiguous U.S. met these criteria; however, a certain percentage were inaccessible, leaving 49,546 lakes in the inference population that the sampled lakes represent. Inference lakes were stratified by state and lake size. Each lake randomly selected for sampling from the inference population was assigned a weight that indicated the number of lakes it represented based on its probability of being selected from the stratified state-size group. These weights were applied to our isotope results to scale the results to the entire inference population (49,546 lakes).

The NLA was focused on assessing biological condition of lakes. Two biological indices were developed for NLA: a planktonic observed : expected (O : E) taxa loss model (Hawkins 2006) and a sediment diatom index of biological integrity (Stoddard et al. 2008). Details of both of these biological indicators can be found in the NLA technical appendix (U.S. EPA 2010). U.S. EPA (2009) classified lakes into three biological condition categories based on the plankton O : E taxa loss model: good ($< 20\%$ taxa loss), fair (20–39% taxa loss), and poor ($> 40\%$ taxa loss). We compare our hydrological indicators with these indices to help assess the usefulness of our indicators in these national assessments.

Water isotope measurements—Lakes were sampled between 08 May 2007 and 18 October 2007, with three lakes sampled in May, 175 lakes in June, 409 lakes in July, 375 lakes in August, 157 in September, and 9 lakes in October. At the deepest part of the lake (where lake depth was measured), a 1-liter sample of water was collected from an integrated sample from the upper 2 m of the lake (or to lake depth if shallower than 2 m) into a completely filled cubitainer with a tightly closed cap. This integrated summer sample of the epilimnion in deep lakes, or integrated sample of the whole or nearly whole water column in shallow lakes, was designed to provide a good representation of the well-mixed portion of the lake for water quality monitoring (U.S. EPA 2010). Samples were shipped overnight to the U.S. EPA water chemistry laboratory in Corvallis, Oregon, for standard chemical analysis, including total nitrogen and phosphorus concentration and chlorophyll *a* (Chl *a*) concentration (U.S. EPA 2009). For 10% of the lakes, duplicate field samples were collected at the same time and shipped. After filtering, a subsample was collected in 20-mL glass vials with polyseal conical inserts within the cap to prevent evaporation. Vials were filled to avoid headspace, and samples were stored cap side down until analysis. Laboratory duplicates were also split on 5% of the samples upon arriving from the field. In 2010, all samples were analyzed for water isotope ratios (δ^2H, δ^{18}O) on a laser absorption water vapor isotope spectrometer (Model 908-0004, Los Gatos Research) located at the Integrated Stable Isotope Research Facility at the Western Ecology Division of the U.S. EPA, Corvallis, Oregon. All δ^2H and δ^{18}O values were expressed relative to Vienna Standard Mean Ocean Water (VSMOW) in parts per thousand (‰),

$$\delta^2\text{H or } \delta^{18}\text{O} = \frac{R_{sample}}{R_{standard}} - 1 \quad (1)$$

where R is the ratio of ^{2}H to ^{1}H atoms or ^{18}O to ^{16}O atoms in the sample and the standard VSMOW. Measurement precision estimates ($\pm$ 1 standard deviation) were determined on both field and lab duplicates and were 0.35‰ and 0.11‰, and 0.27‰ and 0.10‰, for δ^2H and δ^{18}O, respectively. The precision on these duplicate samples were similar to the variance on repeated measures of our internal standards: 0.26‰ and 0.14‰ for δ^2H and δ^{18}O, respectively, representing analytical precision of the instrument. The similarity of precision for field and lab duplicates with analytical precision of the instrument indicates that samples did not evaporate during shipping or storage before analysis.

We calculated deuterium excess (*d-excess*) as an index of how much evaporation has affected the isotopic value of each surface water sample using the following equation (Dansgaard 1964; Clark and Fritz 1997):

$$d\text{-}excess = \delta^2\text{H} - 8\delta^{18}\text{O} \quad (2)$$

The *d-excess* value indicates the influence of kinetic fractionation (evaporation) compared with equilibrium fractionation on water isotopic ratios. The ratio of δ^2H to δ^{18}O equilibrium fractionation factors is approximately 8 under standard atmospheric conditions. Ocean water has an average *d-excess* of 0, whereas the average *d-excess* for precipitation is 10. In terrestrial environments, surface waters with *d-excess* values < 10 are presumed to have undergone some evaporation. Lower *d-excess* values in lakes generally indicate more evaporation.

Isotopic estimation of E : I and lake water residence time—We estimated hydrological metrics from lake water isotopes by applying steady-state mass balance equations that assume that lakes were well mixed and maintain a long-term constant volume (Gibson and Edwards 2002; Gat 2010). Because lakes are dynamic systems, these assumptions are usually not valid. However, applying steady-state equations to dynamic systems such as lakes provides useful quantitative indicators of hydrological conditions at the time of sampling and is more representative of average hydrological characteristics for lakes with longer residence times (Gat 2010). We used the following equations:

$$I_L = Q_L + E_L \quad (3)$$

$$I_L\delta_I = Q_L\delta_L + E_L\delta_E \quad (4)$$

where I_L is inflow (combined surface water, groundwater, and direct precipitation), Q_L is outflow (combined surface water and groundwater), and E_L is lake evaporation. The isotopic values of inflow, outflow, and evaporation fluxes are δ_I, δ_L, and δ_E respectively (which assumes that outflow values are equivalent to measured lake values). δ_L was measured from the lake water sample as described above.

We used precipitation isotopes for δ_I from Water-Isotopes.org, which uses global precipitation oxygen and hydrogen isotope data and empirically calculates the long-term average monthly and annual isotopic composition of precipitation at any location based on algorithms developed by Bowen and Wilkinson (2002) and refined by Bowen and Revenaugh (2003) and Bowen et al. (2005). This assumes that annual averages of precipitation isotopes represent δ_I, which includes all flow paths of water to the lake (surface and groundwater flows and direct precipitation). Clark and Fritz (1997) describe the strong connection between isotopic composition of locally recharged groundwater and mean annual precipitation. Using the weighted mean annual isotopic composition of precipitation to approximate these combined surface and groundwater inflows is appropriate for most hydrogeological settings, except perhaps where the lake is sustained by deep regional aquifers with isotopic values representative of paleowaters or is controlled by distant recharge areas with significantly different isotopic values. Using precipitation isotopes for δ_I also assumes all shifts in water isotopes resulting from evaporation occur in the lake, and not along the flow path to the lake, which can overestimate $E:I$ values in areas with significant wetlands and other lakes within the watershed. We used three methods to determine δ_I. Using Water-Isotopes.org, precipitation isotopes were estimated using both the lake location (point estimate) and the watershed centroid and mean watershed elevation (watershed estimate). Additionally, we estimated precipitation isotope values by calculating the dual isotope slope of the local evaporation line (LEL, slope estimate) and extrapolating back from the lake value to the global meteoric water line (GMWL, $\delta^2H = 8\delta^{18}O + 10$). This LEL slope method allows us to estimate inputs for lakes in which δ_I might not be well represented by precipitation isotope, as mentioned above. The LEL slope (S_{LEL}) was estimated from the following equation assuming that input waters and atmospheric moisture are in isotopic equilibrium (Gat 2010):

$$S_{LEL} = \frac{[\varepsilon^+ + \varepsilon_k]_2}{[\varepsilon^+ + \varepsilon_k]_{18}} \tag{5}$$

where ε^+ is the equilibrium enrichment factor and ε_K is the kinetic enrichment factor. The values in the numerator are for δ^2H, and the denominator for $\delta^{18}O$. We estimated ε^+ using temperature data and the equations from Horita and Wesolowski (1994). ε_K is influenced by relative humidity and boundary layer conditions and can be estimated by $\varepsilon_K = C_K(1 - h)$, where C_K was set to 14.2‰ for oxygen and 12.5‰ for hydrogen (Gibson and Edwards 2002). Because no single method for estimating δ_I was uniformly good across the entire range of lakes, the δ_I value used was the one that minimized the difference between $E:I$ estimated independently from the two isotopes ($\delta^{18}O$ and δ^2H), which minimized the error associated with estimating δ_I. We also conducted sensitivity analyses for the variation between estimates.

The isotopic value of evaporating water, δ_E, was estimated using the Craig–Gordon model for open-water evaporation (Craig and Gordon 1965):

$$\delta_E = \frac{(\delta_L - \varepsilon^+)/\alpha^+ - h\delta_A - \varepsilon_K}{1 - h + \varepsilon_K} \tag{6}$$

where h is atmospheric relative humidity, δ_A is the isotopic composition of atmospheric vapor, α^+ is the equilibrium fractionation between liquid and vapor ($\alpha^+ = 1 + \varepsilon^+$). We assumed that δ_A was in isotopic equilibrium with evaporation flux-weighted precipitation (i.e., annual estimates derived from monthly precipitation isotopes weighted by monthly potential evapotranspiration [PET]; *see* below for PET details).

Combining Eqs. 4 and 6 and substituting Q_L with $I_L - E_L$, we derive the following equation for lake $E:I$ (Gibson and Edwards 2002; Gibson and Reid 2010):

$$\frac{E_L}{I_L} = \frac{\delta_I - \delta_L}{m(\delta^* - \delta_L)} \tag{7}$$

where $m = (h - \varepsilon_K - \varepsilon^+/\alpha^+)(1 - h + \varepsilon_K)^{-1}$ and $\delta^* = (h\delta_A + \varepsilon_K + \varepsilon^+/\alpha^+)(h - \varepsilon_K - \varepsilon^+/\alpha^+)^{-1}$. We estimated lake water τ from the $E:I$ estimates and annual estimates of PET from the lake surface for E in the following equation (Gibson et al. 2002):

$$\tau = \left[\frac{E}{I}\right]\frac{V}{E} \tag{8}$$

where V is lake volume. We used the method described by Hollister and Milstead (2010) for estimating lake volume, which uses maximum depth measurement and a geographic information system (GIS) layer of lake shoreline. Monthly climate data (precipitation, dew point, mean maximum and minimum temperatures) for 2007 were obtained for each lake using the Parameter-elevation Regressions on Independent Slopes Model algorithm (Daly et al. 2008). Monthly PET was estimated from temperature data using the Hamon equation (mm month^{-1}) according to Wolock and McCabe (1999). $E:I$ and τ values were estimated for both $\delta^{18}O$ and δ^2H, and the average value was used. Because very low values of $E:I$ can lead to unrealistically large estimates of I, we substituted annual precipitation for I when estimates of I were greater than annual precipitation in the watershed ($\sim$ 100 lakes). As an independent estimate of τ, we used runoff estimates from McCabe and Wolock's (2011) water balance model generated from 2007 precipitation and temperature data (τ_m). The isotope-derived τ will be denoted $\tau_{E:I}$.

All statistical analyses were conducted using R (version 2.15.2, 2012-10-26, The R Foundation for Statistical Computing, www.r-project.org). Weighted analysis was used to analyze and scale the sampled lake data (1028 lakes) to the entire inference population of lakes (49,546

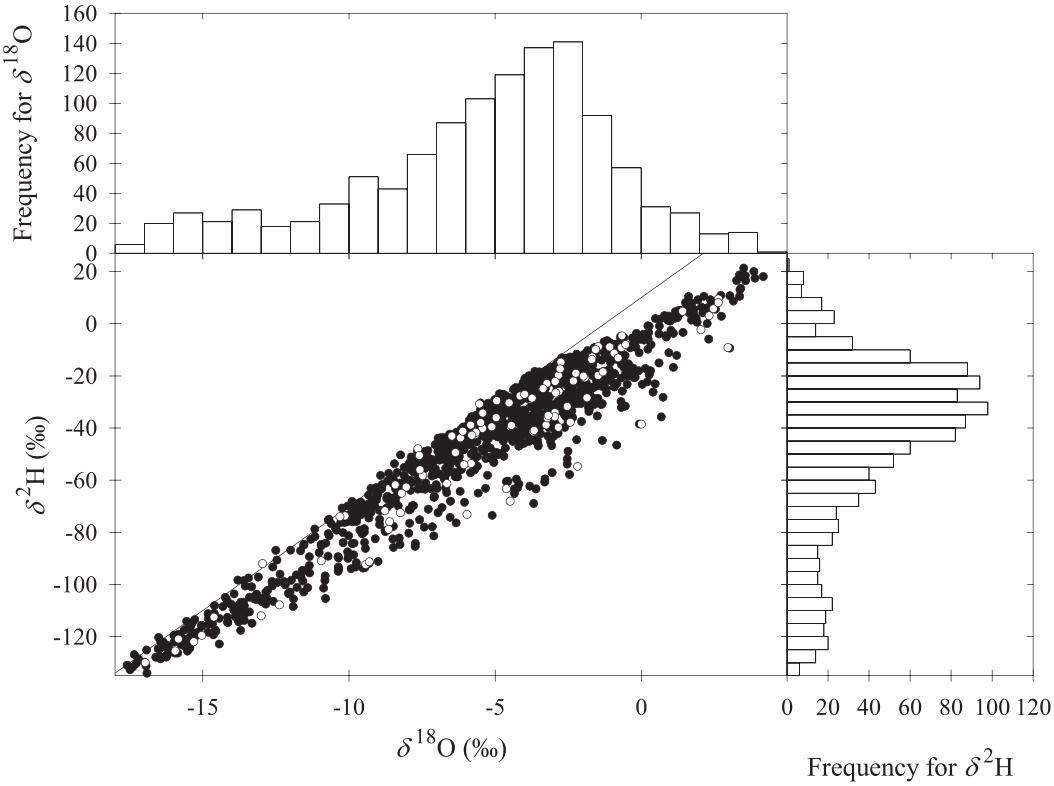

Fig. 1. Values of δ^{18}O and δ^2H for all lakes sampled in the 2007 National Lakes Assessment along with frequency distributions for the range of isotope values. The white points are the 10% of lakes sampled a second time. The line in the dual-isotope plot is the GMWL.

lakes) using the lake weights assigned in the NLA probability-based survey design (*see* above for details). We summarized the data using lake weights with the R packages plyr and Hmisc. A combination of weighted analysis of variance and weighted linear regressions was used to determine trends and significant groupings within the data and is specified within the results section. We also used Kruskal–Wallis and Theil–Sen nonparametric tests in the R packages pgirmess and zyp to confirm patterns, but these tests are not available using weighted statistics. Nitrogen fertilizer loading to the lake watersheds was estimated using the data synthesized by Sobota et al. (2013) based on average (1990–2001) annual U.S. county-level N fertilizer applications. We provide spatial maps of the isotopes and $E:I$ largely to show general trends rather than to model the spatial variation explicitly. Therefore, we simply used ordinary kriging in ArcGIS (five nearest neighbors and no underlying trend) to interpolate values. When values are aggregated by region, we used nine aggregated ecoregions used in U.S. EPA's NLA and described in the NLA technical appendix (U.S. EPA 2010; Peck et al. 2013).

Results

In the summer of 2007, lake water isotopes ranged from 4.2‰ to −17.6‰ for δ^{18}O and 21.3‰ to −134‰ for δ^2H with *d-excess* values ranging from 15.6‰ to −41.2‰ (Fig. 1). The median, weighted by sampling probability, was −4.2‰ and −39.9‰, respectively, for δ^{18}O and δ^2H and −3.45‰ for *d-excess*. Ninety-five percent of lake waters plotted below the GMWL ($\delta^2H = 10 + 8\delta^{18}O$; Fig. 1) indicating the evaporated nature of lakes during the summer (*d-excess* 95th weighted percentile = 9.6‰). All lakes with δ^{18}O values greater than −3‰ and δ^2H values greater than −10‰ were below the GMWL. Lake water isotopic values were more enriched than estimated local precipitation isotopic values, with median LEL of 5.1.

The spatial distribution of lake water δ^{18}O values resembles the spatial pattern of precipitation isotopes (Bowen and Wilkinson 2002; Bowen and Revenaugh 2003), with most heavy isotope–enriched lakes located in the southeast and the most heavy isotope–depleted lakes located in the western mountain regions (Fig. 2A). The *d-excess* values were highest (indicating low evaporation) in the northeastern U.S. and other mountainous regions, whereas the lowest (high evaporation) were in the upper Midwest and southwestern U.S. (Fig. 2B). Surprisingly, *d-excess* values were also high in the lower Midwest, but 2007 was a particularly wet summer for that region.

Whereas most lakes were sampled only once during the summer, 10% (95 lakes) were sampled twice on different dates and were used to evaluate the influence of seasonal variation on our hydrologic estimates. The δ^{18}O and δ^2H values of lakes fluctuated seasonally in response to variations in the isotopic composition of precipitation and snowmelt and because of evaporative enrichment that occured over the open-water season. In snow-dominated

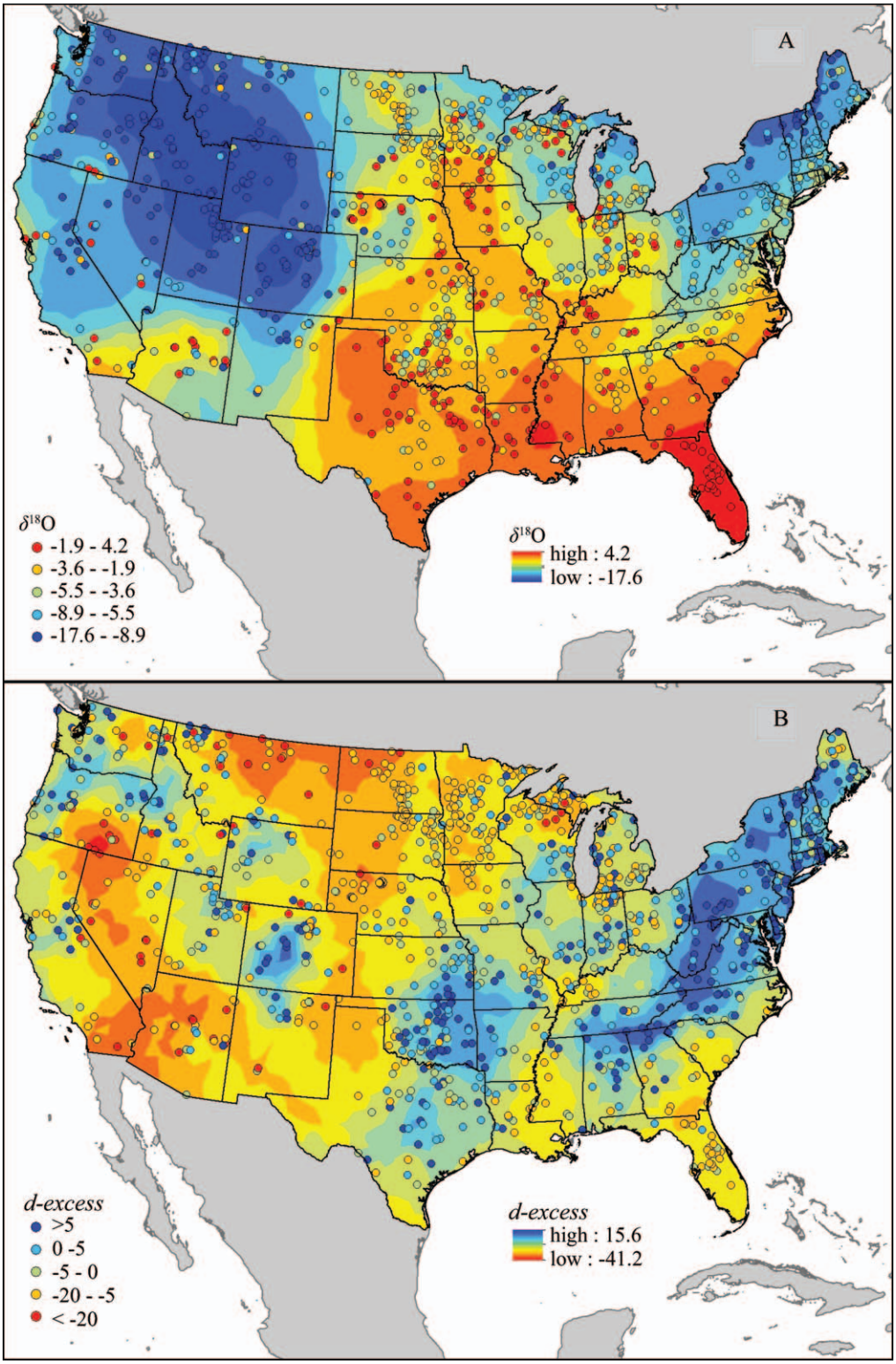

Fig. 2. Isocapes of (A) $\delta^{18}O$ and (B) *d-excess* of lake waters. Each circle represents a sampled lake in the 2007 National Lakes Assessment.

portions of the country, this seasonality included minimum $\delta^{18}O$ and $\delta^{2}H$ values after the influx of snowmelt following the spring freshet, followed by progressive evaporative enrichment over the open-water season (Stets et al. 2010). In other regions of the country, the seasonal cycle in lake isotope values was likely dominated by evaporative enrichment during the summer and early fall. All of the 2007 samples were collected between May and October,

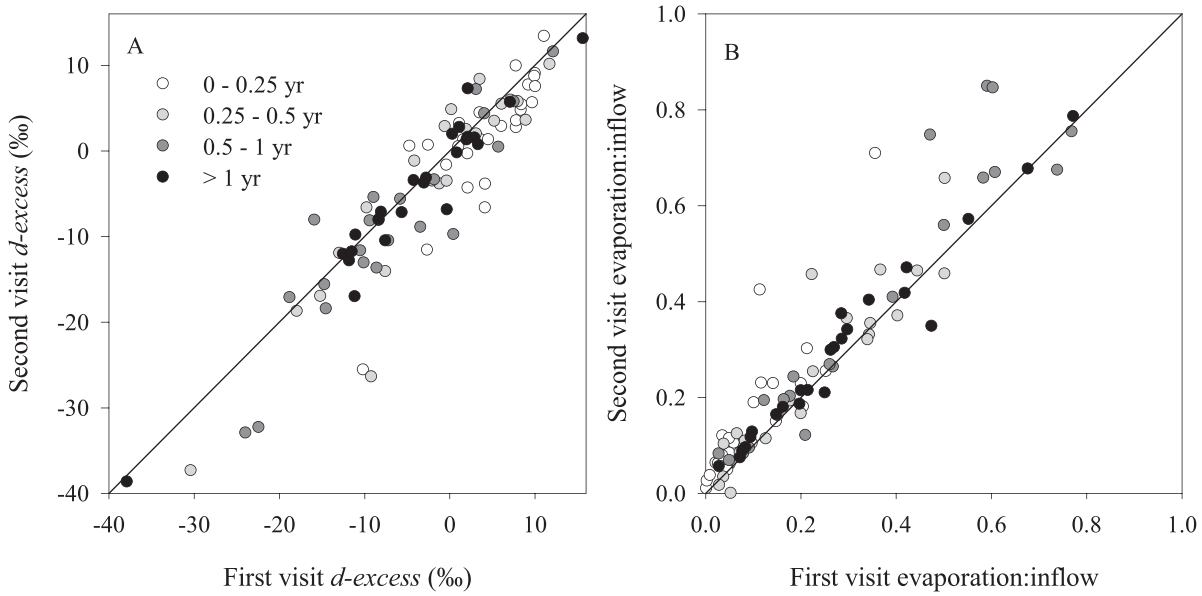

Fig. 3. A comparison between the first and second visit to a lake for (A) *d-excess* and (B) $E:I$. The line is the 1 : 1 line. Shading of circles indicates variation in residence time.

with the majority (70%) collected during July and August. Consequently, these samples should represent intermediate evaporative enrichment for each lake. As expected, the repeat sampling produced $\delta^{18}O$ and $\delta^{2}H$ values that were significantly greater by an average of 0.6‰ and 3.0‰, respectively, during the second visit, and *d-excess* values were significantly lower by an average of 1‰ (Wilcoxon signed-rank test, $p < 0.001$ for all tests) consistent with the greater evaporative enrichment that would occur as the summer season progressed. However, these shifts between visits were very small relative to the range of values and the variance among sites (Fig. 1). Because all samples were integrated over the upper 2 m at the deepest portion of the lake, within lake variability related to sampling location should be minimized. Signal to noise ratios (variance among lakes : mean variance between visits) were 29.3, 72.6, and 8.7 for $\delta^{18}O$, $\delta^{2}H$, and *d-excess*, respectively, where values > 10 are considered excellent indicators for detecting differences among sites relative to the variance within a site (Kaufmann et al. 2014). Using root mean squared errors (*RMSE*) between visits as a measure of precision, precision values were 0.8‰, 3.8‰, and 3.1‰, whereas the ranges are over 20‰, 150‰, and 55‰ for $\delta^{18}O$, $\delta^{2}H$ and *d-excess*, respectively. For *d-excess*, a mean shift of only 1‰ was found with repeat values clustering closely around the 1 : 1 line (Fig. 3A). Additionally, the rank order of lakes between the first and second visit was highly correlated (Spearman's rank correlation $\rho > 0.9$ for *d-excess*, $E:I$, and $\tau_{E:I}$). In most cases, these repeat values were too isotopically similar to determine a reasonable LEL to compare with the LEL slope estimated by Eq. 5. $E:I$ differences between visits were also small, with a median increase in $E:I$ of 0.03 and clustering around the 1 : 1 line (Fig. 3B). The median $E:I$ difference tended to increase with shorter residence times, increasing from 0.02 for lakes with residence times > 1 yr to 0.04 for lakes with residence times < 0.25 yr. Moreover, the $E:I$ difference between visits tended to get larger as the time between repeat sampling dates increased: lakes repeated 100 d after the initial sampling had a mean difference of 0.1 in $E:I$. These repeat measurements indicate that although evaporation does tend to increase through the summer and increase more for lakes with short residence times, these within-lake changes were relatively small compared with the range of $E:I$ values for the lake population as a whole. The precision (*RMSE*) of $E:I$ values was $\pm$ 0.065. The signal to noise ratio for $E:I$ was 11.5, indicating that the variance among lakes is 11.5 times greater than the variance between visits. Residence time also tended to increase during the summer, with a median increase of 0.06 yr with a *RMSE* of 0.23 yr, and a signal to noise ratio of 10.6. Thus, although both $E:I$ and τ tended to increase during the summer, estimating $E:I$ and τ from one visit during the summer was a viable approach for assessing the distribution of the summertime hydrologic status of the nation's lakes for 2007 using the statistical survey approach.

Besides the measured lake water isotope compositions, estimates of $E:I$ are also sensitive to the estimated parameters used in Eqs. 6 and 7 and, in particular, to estimates of the isotopic value for lake inflows δ_I, which includes all inflows into the lake (surface water, groundwater, and direct precipitation) and assumed that no evaporation occurred before the water entered the lake. We estimated the isotopic value of lake water inflow using three different methods outlined above. The point and watershed method estimates of precipitation isotopes from WaterIsotopes.org gave very similar δ_I estimates of $E:I$ (median 0.21 vs. 0.20, mean 0.30 vs. 0.28, standard deviations 0.37 vs. 0.38, respectively), whereas the slope method estimates were generally higher (median 0.26, mean 0.36, standard deviation 0.31), because δ_I estimates from

Table 1. Spearman's rank correlation (ρ, upper matrix) and Pearson's correlation coefficients (r, lower matrix) between $E:I$ values estimated using three different methods for selecting the isotope values for lake inflow. Point method uses the lake location and elevation; the watershed method uses the watershed centroid and mean elevation in WaterIsotopes.org for predicting precipitation isotopes. The slope method uses the estimated local evaporation line predicted from climate data (*see* Methods for details).

	Point $E:I$ estimates	Watershed $E:I$ estimates	Slope $E:I$ estimates
Point $E:I$ estimates	—	0.94	0.87
Watershed $E:I$ estimates	0.96	—	0.80
Slope $E:I$ estimates	0.73	0.84	—

the LEL slope were generally lower than those from WaterIsotopes.org. Nevertheless, the $E:I$ correlations between the three estimates were all very high (Table 1), indicating that although the $E:I$ values may shift somewhat from method to method, the relative ranking of a particular lake is very similar. Equations 6 and 7 were solved independently for each isotope. Although the $E:I$ estimates based on δ^2H tended to be higher than those based on δ^{18}O (median 0.21 vs. 0.18), the overall rank order of lakes was very similar between isotopic estimates (Fig. 4). $E:I$ values used throughout were those based on δ_I values that gave the most similar $E:I$ values between oxygen and hydrogen isotopes, and δ_I values were not higher than the measured lake isotope values. We averaged the estimates from the two isotopes for the final $E:I$ values.

During the summer of 2007, lake $E:I$ values ranged from 0 to 1.13, and the distribution was positively skewed with a median of 0.25 and a mean of 0.32 (Fig. 5A). For half of the lakes, $< 25\%$ of the water entering the lake leaves through evaporation. Only 25% of lakes have $E:I$ values > 0.5. The proportion of water that leaves through evaporation decreases with increasing lake depth (Fig. 6A). Shallow lakes (< 2 m measured at the deepest point in the lake, 22% of lakes) have the widest range of $E:I$, with a weighted median of 0.42, and have significantly greater $E:I$ values than deeper lakes. Lakes with maximum depth > 10 m (14% of lakes) have a weighted median $E:I$ of 0.10, which was significantly lower than shallower lakes. Maximum lake depth was more strongly correlated with $E:I$ than was lake volume or lake area ($\rho = -0.41$ for depth vs. $\rho = -0.25$ and -0.12 for volume and area, respectively, Spearman's rank; all $p < 0.001$), or even volume per area, although this was closely correlated with maximum depth ($\rho = -37$, Spearman's rank; $p < 0.001$).

Other important factors determining the variation in $E:I$ were climate (precipitation, temperature, and relative humidity) and watershed size. Not surprisingly, the precipitation volume that falls within a lake's watershed was inversely correlated with $E:I$ because it represented a rough approximation of I ($\rho = -34$, $p < 0.001$, Spearman's rank). Precipitation volume was the second most important

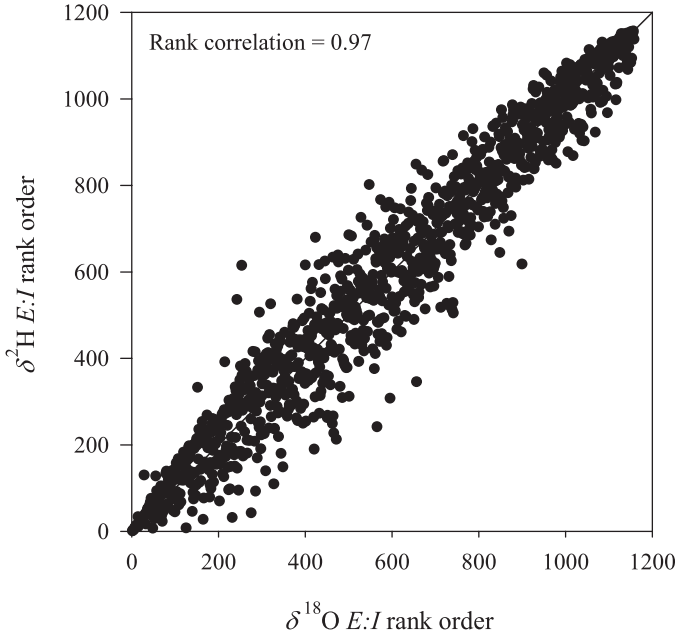

Fig. 4. Rank correlation between $E:I$ values calculated using either δ^{18}O or δ^2H values. The line is a 1 : 1 line.

variable explaining variation in $E:I$ after lake depth. The spatial distribution of $E:I$ resembled that of *d-excess* and was largely driven by climate factors, whereas the variation within a region was driven by lake-specific factors, such as depth and watershed size (Fig. 7). Low values of $E:I$ were found in mountain ecoregions with high precipitation and low evaporation rates: the northern Appalachians ecoregion with a weighted median $E:I$ value of 0.11, the western mountains median of 0.19, and a southern Appalachians median of 0.17. Additionally, low values of $E:I$ were found in the southern and coastal plains ecoregions, with median values of 0.16 and 0.23, respectively. These areas were lower than one might expect as a result of high precipitation in that area for 2007. The xeric ecoregion was also not as high as might be expected based on precipitation and evaporative demand, with a median value of 0.21 and a mean of 0.28, because basin sizes were an order of magnitude larger in this ecoregion and most xeric region lakes received waters from the southwestern mountains, so inflow tends to be high. The three ecoregions with the highest weighted median $E:I$ values were the temperate plains, with a median of 0.51, the northern plains, with 0.42, and the upper Midwest, with 0.32—all ecoregions with relatively high evaporative demand and low precipitation.

It is important to note that isotope mass balance cannot be used to estimate lake water τ for lakes with no detectable evaporative enrichment signal in their isotopic composition. Additionally, when $E:I$ estimates were very small, calculations of I could be unrealistically large (larger than precipitation inputs). When I was greater than precipitation inputs to the watershed, we substituted annual precipitation volume for I in estimating τ (V:I). For the summer of 2007, estimates of $\tau_{E:I}$ range from essentially 0 to just > 10 yr with two outlier lakes being > 20 yr (21 and 146 yr),

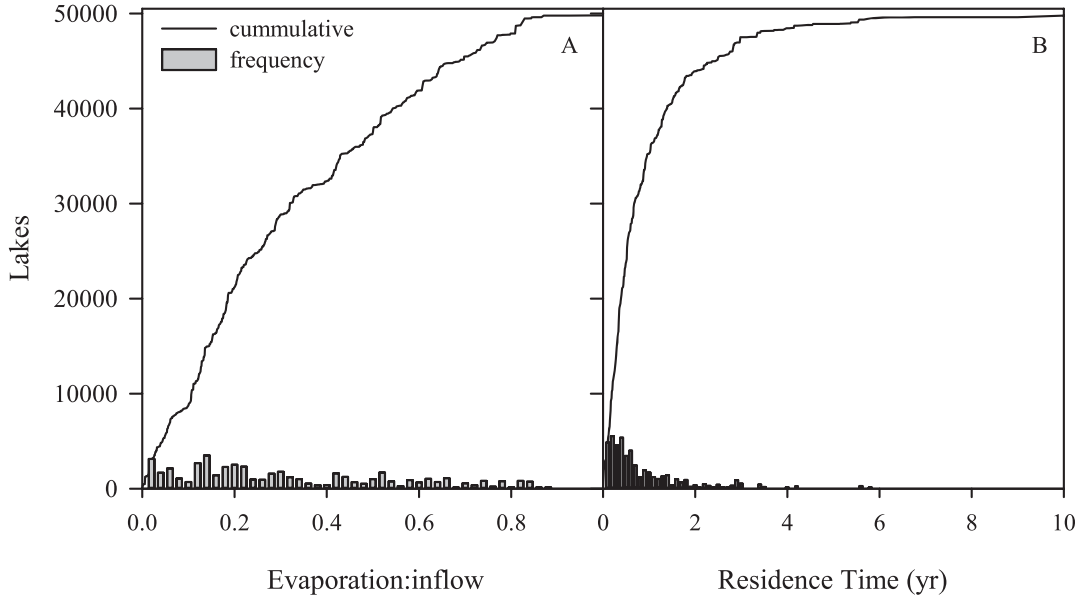

Fig. 5. Cumulative and frequency distributions of (A) $E:I$ and (B) lake water residence time scaled to the entire NLA inference population of lakes within the U.S.

again with a positively skewed distribution (Fig. 5B). We estimated that 50% of lakes have a residence time of < 0.52 yr and a mean value of slightly < 1 yr. Ninety-five percent of lakes had water residence times < 3.7 yr in the summer of 2007. Estimates of $\tau_{E:I}$ correlated with τ_m estimates based on McCabe and Wolock's mass balance runoff model ($\rho = 0.70$, Spearman's rank; $p < 0.001$). However, τ_m had a lower mean and median (0.8 yr and 0.26 yr, respectively).

Of the driving factors that could explain the variance in lake water residence time ($\tau_{E:I}$), lake depth and the volume of precipitation that falls within the watershed had the strongest correlation ($\rho = 0.50$ and -0.31, respectively, Spearman's rank; $p < 0.001$). We excluded driving factors that were used to estimate $\tau_{E:I}$: $E:I$, lake volume, and lake evaporation (Eq. 8). Precipitation volume is a close approximation of I and is influenced by the size of the watershed and precipitation amount. Interestingly, the correlation between $\tau_{E:I}$ and lake depth was the strongest of all climate or lake parameter correlations. Lake water residence time increased with maximum lake depth (Fig. 6B). Lakes shallower than 2 m had a mean and median $\tau_{E:I}$ of 0.37 and 0.34 yr, respectively, whereas the deepest lakes (> 20 m) had a mean $\tau_{E:I}$ of 3.8 yr and a median of 2.25 yr. Because of the strong influence of lake depth and watershed area (through its effect on precipitation volume) on $\tau_{E:I}$, the spatial patterns for $\tau_{E:I}$ were not as robust as for $E:I$, but some trends were noted. Lake water residence times were the lowest in the coastal plains ecoregion, with a median of 0.17 yr and a mean of 0.27 yr. The longest residence times were located in the upper Midwest, with a median value of 1 yr and a mean value of 1.6 yr.

The chemical condition of lakes was strongly related to the isotopic estimates of $E:I$ (Table 2). Total nitrogen concentration increased with increasing $E:I$ for both natural and man-made lakes (Fig. 8). $E:I$ alone explains 24% of the variation in total nitrogen (log scale) within lakes across the U.S. (weighted linear regression, $R^2_{\text{adjusted}} = 0.24$, $F_{1,1027} = 334$), which was a similar amount of variance explained as fertilizer loading onto the landscape. Together, fertilizer loading and $E:I$ explain 41% of the variation in lake nitrogen concentration (weighted linear regression, $R^2_{\text{adjusted}} = 0.41$, $F_{1,1026} = 356$). The relationship between lake nitrogen concentration (log scale) and $E:I$ was stronger for natural lakes, with a slope of 3.3 (3.0–3.6, 95% confidence interval, Theil–Sen estimate of slope) compared with man-made lakes with a slope of 2.1 (1.7–2.4, 95% confidence interval, Theil–Sen estimate of slope). $E:I$ was also positively correlated with total phosphorus concentration and Chl *a* content (Table 2). Lake water residence times (both $\tau_{E:I}$ and τ_m) were negatively correlated with chemical concentrations, but the correlations were much weaker than for $E:I$. The negative correlations were also stronger with the isotope-derived $\tau_{E:I}$ compared with the modeled τ_m.

We also found that lakes in poor biological condition, as determined by the NLA, had higher $E:I$ values than lakes in good biological condition (Fig. 9; Table 2). As shown earlier (Fig. 7), $E:I$ varied by region, with the plains and coastal areas being more isotopically enriched than either the western region or eastern highlands. Consequently, we split these three aggregated ecoregions for comparing lakes with different biological condition. Within each of the three ecoregions, lakes in poor biological condition were significantly more evaporated than lakes in good condition where condition was based on O:E plankton species (Fig. 9). $E:I$ was negatively correlated with both indicators of biological condition used in the NLA (Table 2). Lake water residence times were not consistently correlated with the biological indices, but tended to be weakly positively correlated.

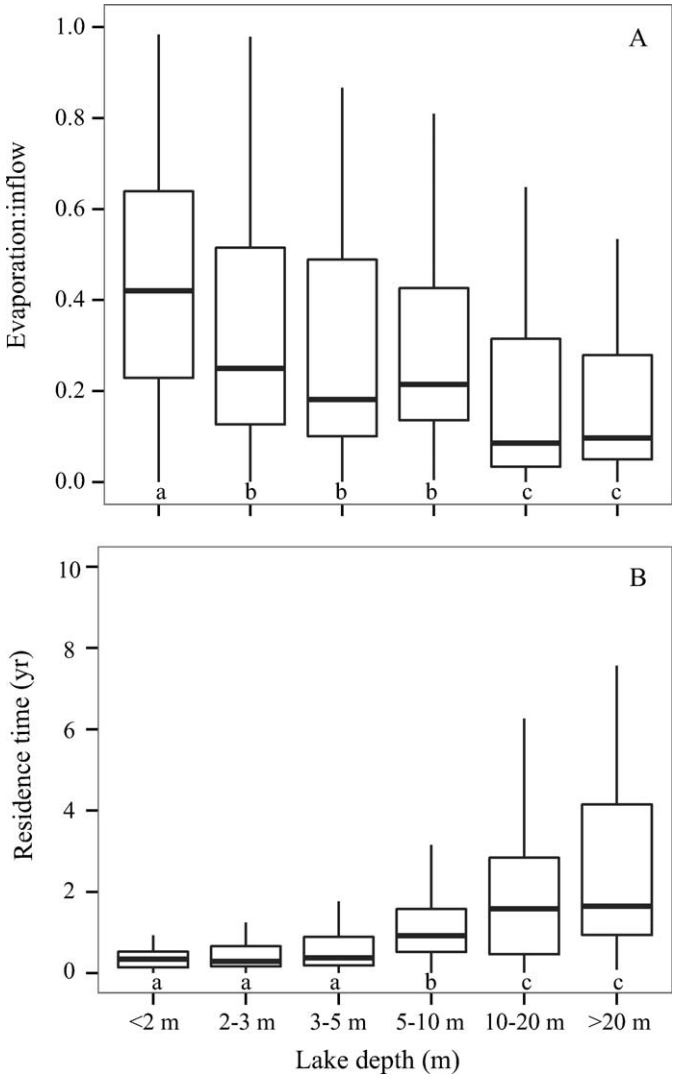

Fig. 6. The box plots of (A) $E:I$ values and (B) lake water residence time ($\tau_{E:I}$) separated by maximum lake depth. The box represents the 25th to 75th percentile, and the center band is the median value. Whiskers represent the 5th and 95th percentiles. The distributions have been scaled to the entire inference population of lakes in the U.S. ($\sim$ 50,000) by using the sampling probability weights (*see* Methods for details). Depth categories with different letters are significantly different from each other (α = 0.05, weighted analysis of variance, partial *F*-test, and nonweighted, nonparametric Kruskal–Wallis rank sums test; results were the same for both tests).

Discussion

By analyzing $\delta^{18}O$ and $\delta^{2}H$ of lake water samples collected as part of the U.S. EPA's 2007 NLA, we estimated summertime $E:I$ and residence time for $>$ 1000 lakes distributed across the nation. We scaled those results to estimate the 2007 summertime distribution of these parameters for the entire inference population of nearly 50,000 lakes based on the NLA probabilistic survey design (Olsen et al. 2009; Peck et al. 2013). Although isotopes do provide estimates of $E:I$ and $\tau_{E:I}$ that are integrated over water residence time, both variables are dynamic within lakes; thus, these estimates provide a snapshot of the hydrological condition of lakes within the U.S. for the summer of 2007. While it would be problematic to estimate the annual average hydrologic condition of individual lakes based on single samples used in the NLA, the seasonal variability in $E:I$ and τ becomes part of the error around the estimated population distribution using the NLA survey design (Peck et al. 2013). The summertime distributions of both $E:I$ and $\tau_{E:I}$ were positively skewed (Fig. 5). Seventy-five percent of lakes have greater flow-through than evaporation ($E:I<0.5$), and residence time of $<$ 1 yr. Regional differences in $E:I$ and $\tau_{E:I}$ were driven primarily by climate (Fig. 7), and we also found variation relating to depth of the lake (Fig. 6), with deeper lakes having lower evaporation and longer residence times than shallower lakes. Watershed area was also an important driver of both variables through its influence on the volume of water entering a lake. Lake nitrogen concentration was strongly related to $E:I$ (Fig. 8; Table 2), with higher nitrogen concentrations found in lakes with greater $E:I$. Lake nitrogen concentration was negatively correlated to $\tau_{E:I}$, although more weakly than $E:I$. We also found an association of $E:I$ with biological condition of a lake (Fig. 9), likely related to the nutrient relationship because nutrients can be stressors to lake biology (Van Sickle 2013). Our results demonstrate that including lake water isotope measurements in large-scale, spatially extensive monitoring programs is a practical and inexpensive way to improve our understanding of lake hydrological characteristics at the time of assessment and aids in understanding the reasons for lake impairment at the national scale.

Regardless of the many assumptions, estimating $E:I$ from isotopes measured in a single representative sample provides a good first approximation for lake $E:I$ in the context of the national assessment, and represents the distribution of hydrologic conditions for lakes in the summer of 2007 within the U.S. It is important to note that these $E:I$ and τ distributions do not represent mean annual values, but summertime values in 2007 when the assessment was made. $E:I$ values do tend to increase seasonally as evaporative demand and precipitation change (Gibson et al. 2002; Gibson and Reid 2010), but the degree of change we found within a lake over the summer sampling period was relatively small compared with the distribution of $E:I$ in lakes across the nation (Fig. 3), with a signal to noise ratio of 11.5. With $E:I$ precision of 0.065 (*RMSE*), the minimum $E:I$ difference needed between two lakes based on one sample before the lakes can be considered different in summertime $E:I$ was estimated as $1.96(RMSE)(2n)^{1/2} = 2.77(RMSE)$ (Kaufmann et al. 2014), which gives the 95% confidence interval (0.18). Thus, we found that the relative ranking of a lake's $E:I$ within the national assessment was robust over the summer sampling season. Another sensitive parameter was the isotopic value of water flowing into a lake (Wolfe et al. 2007; Yuan et al. 2011). The best method might be to have direct isotopic measures of surface waters feeding a lake, but this was not part of the 2007 NLA sampling and would not account for potential groundwater inflow. Use of weighted mean

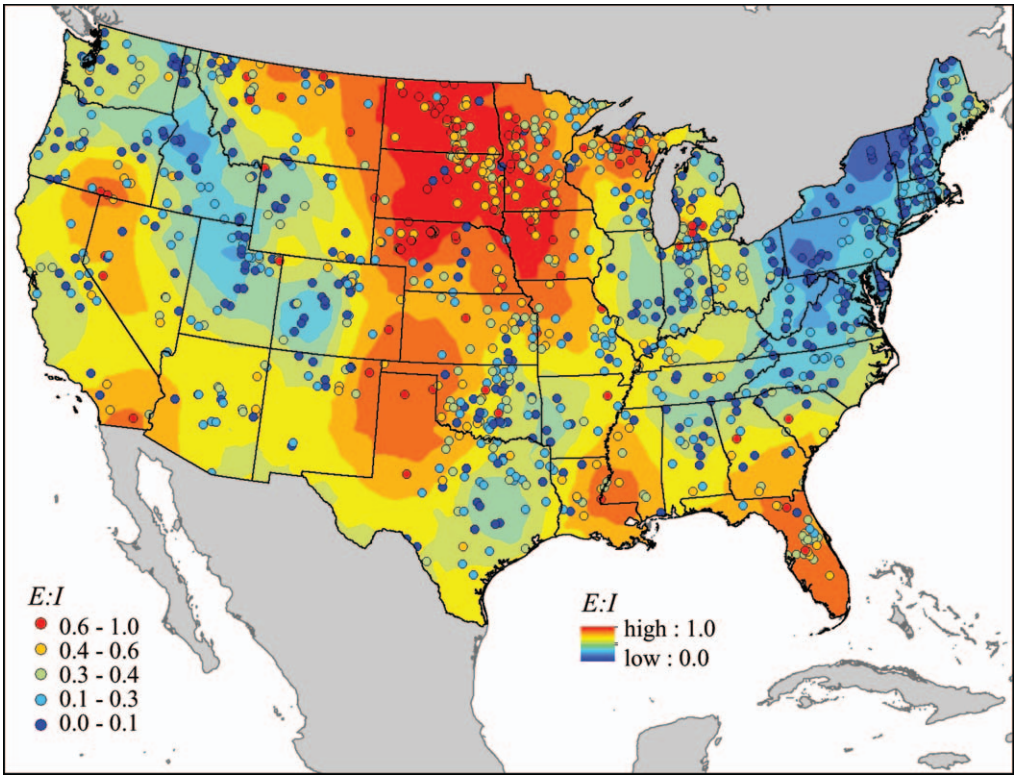

Fig. 7. Map of lake $E:I$.

annual precipitation not only represents the immediate direct inputs to lakes through precipitation and surface flows, but should also be representative of groundwater inputs in most cases because groundwater is mainly derived from local recharge by precipitation (Clark and Fritz 1997). Estimates of precipitation isotopes was the most logical way to estimate δ_I, and the estimates generated by algorithms like those used by WaterIsotopes.org are continuing to improve as more precipitation datasets become available and as conceptual and numerical models of climate controls on the isotopic composition of precipitation continue to improve. The LEL slope method did help account for lakes in which estimates of precipitation isotopes from WaterIsotopes.org did not adequately reflect δ_I. However, using precipitation isotope estimates assumes that no evaporation occurs prior to the water entering the lake, which would overestimate $E:I$ values in areas with wetlands or other lakes along the flow path. We approached estimating δ_I by using three methods (*see* Methods for details). Whereas the two estimates from WaterIsotopes.org produced similar $E:I$ values, the LEL slope estimation method using Eq. 5 produced greater $E:I$ values, because this method produced more depleted δ_I values than WaterIsotopes.org. Nevertheless, the relative rank of a lake was very similar regardless of the method used for δ_I (Table 2). Another approach to reduce uncertainty was making input parameter assumptions that reduced the difference between $E:I$ estimated for $\delta^{18}O$ and δ^2H. For example, we assumed that atmospheric moisture was in isotopic equilibrium with evaporative flux-weighted precipitation because this assumption lowered the difference between the oxygen and hydrogen $E:I$ estimates, compared with when atmospheric moisture was assumed to be in isotopic equilibrium with precipitation-weighted precipitation. Other studies have found similar results concerning δ_A equilibrium (Wolfe et al. 2007; Gibson et al. 2008). Although these assumptions may shift $E:I$ estimates for a given lake, they did little to the rank order of lakes across the nation (Fig. 4), giving us confidence in these $E:I$ estimates based on a single representative and integrated

Table 2. Spearman's rank correlation coefficients (%) between hydrological measures and water quality parameters. $\tau_{E:I}$ and τ_m represent residence time estimated using stable isotopes and runoff modeling, respectively. Correlations in bold are significant ($p < 0.01$).

	N(μg L^{-1})	P(μg L^{-1})	Chl a(μg L^{-1})	Plankton O:E	Diatom IBI*
$E:I$	**53.0**	**38.8**	**32.0**	**−26.1**	**−28.9**
Residence time ($\tau_{E:I}$)	**−8.8**	**−25.7**	**−27.5**	6.3	5.0
Residence time (τ_m)	−6.2	**−20.0**	**−21.8**	−3.4	**7.9**

* Diatom IBI, index of biological integrity.

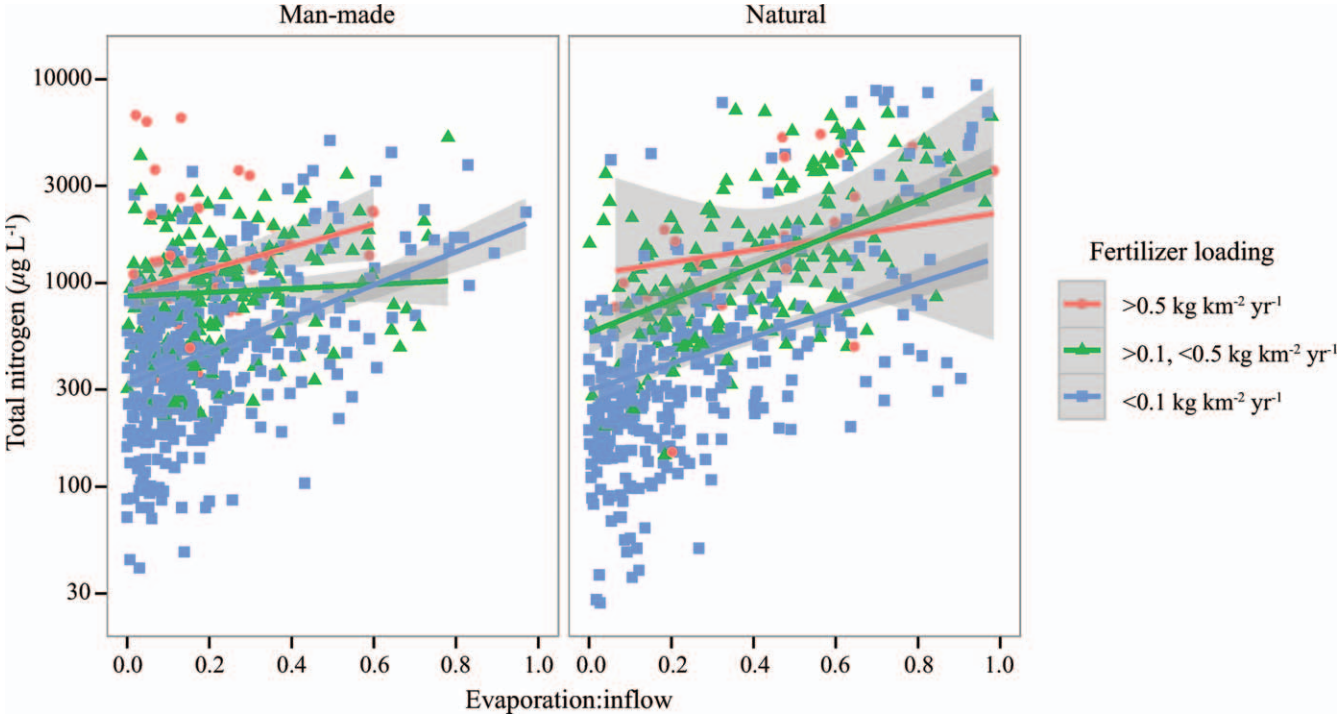

Fig. 8. The relationship between lake $E:I$ values and the natural log of total nitrogen content in the lake for man-made and natural lakes. Lakes were categorized on the basis of nitrogen fertilizer loading to the watersheds (based on data synthesized by Sobota et al. [2013]). The lines are linear regression using lake weights to scale results to the entire population of lakes. Grey areas around lines represent 95% confidence intervals for the regression.

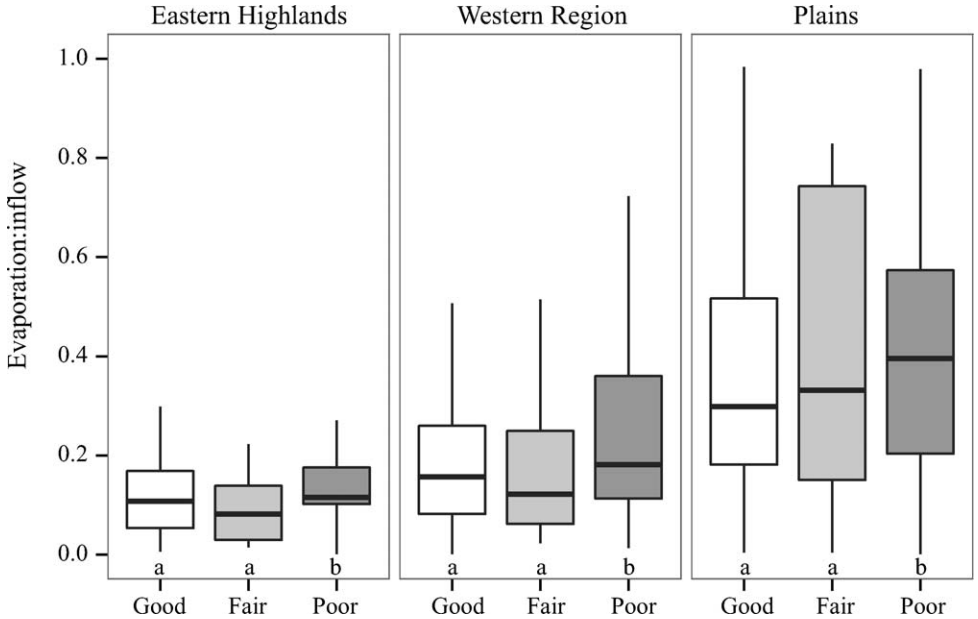

Fig. 9. Box plot distributions of $E:I$ between lake condition classes based on O:E plankton species for three combined ecoregions. The distributions have been scaled to the entire lake population in the U.S. by using the sampling probability weights (*see* Methods for details). $E:I$ values for condition classes with different letters are significantly different from each other (α = 0.05, weighted analysis of variance, partial F-tests, and nonweighted, nonparametric Kruskal–Wallis rank sums test; results were the same for both tests).

sample from a lake for the purposes of a spatially extensive national lakes assessment.

Estimates of residence time introduce more potential sources of error because we needed to estimate lake volume and annual evaporation from the lake (Eq. 8). Lake volume can be particularly challenging to estimate (Sobek et al. 2011). The method developed by Hollister and Milstead (2010) used maximum depth measurements made in the field (maximum measurable depth was 50 m) and GIS shoreline information, so although these estimates are more accurate than techniques that assume a conical shape, they still introduce a level of error. Our estimate of precision based on repeat visits was ± 0.23 yr (*RMSE*), and the minimum difference needed to detect a difference between two lakes based on one sample was 0.64 yr. Our isotope-based estimates of τ were correlated with more traditional estimates of τ using modeled runoff, but the isotope method tended to predict longer residence times than the runoff method. In comparing $\tau_{E:I}$ and τ_m with previous regional estimates of τ calculated from measured lake bathymetry and regional runoff values (Lindthurst et al. 1986), the values are similar for the northeastern U.S., with median $\tau_{E:I}$ and τ_m values of 0.27 and 0.21 yr, respectively, compared with 0.20 yr for U.S. EPA's 1986 regional estimate. Median values diverged more for τ estimates for the upper Midwest, with median $\tau_{E:I}$ and τ_m values of 1.04 and 0.69 yr, respectively, compared with the 1986 estimate of 0.48 yr.

We found that lake water isotopes, $E:I$ and $\tau_{E:I}$ values varied with climatic region across the U.S. (Figs. 2, 7). Our lake $\delta^{18}O$ and $\delta^{2}H$ values ranged approximately two thirds the range of a global survey of large lakes (Jasechko et al. 2013), with our survey being more limited on the enriched end of the range. Not surprisingly, the $\delta^{18}O$ spatial pattern superficially reflected the spatial pattern of precipitation and river waters across the U.S. (Kendall and Coplen 2001; Bowen and Wilkinson 2002; Bowen and Revenaugh 2003), but with significantly enriched values in the southwest and central to upper Midwest, where $E:I$ was highest. As might be expected given the spatial extent of our survey, the range of $E:I$ values estimated for the contiguous U.S. (0–1) was greater than those observed in regional studies such as for northern Canada, where 255 lakes ranged from 0 to 0.7 with a median of 0.11 (Gibson and Edwards 2002) and from the Tibetan Plateau, were values ranged from 0.1 to 0.75 with a mean of 0.52 for 27 lakes (Yuan et al. 2011). However, Wolfe et al. (2007) found a much broader range in the Peace–Athabasca Delta in Alberta, Canada, ranging from 0 to > 2 with a median of 0.7. They classified their lakes into flow-through lakes, where 60% or more of the lake inflow flows back out of the lake ($E:I < 0.4$); restricted-drainage lakes, where 40% or more of lake inflow leaves through evaporation ($0.4 \leq E:I < 1$); and closed-basin lakes, where all lake inflow leaves through evaporation ($E:I \geq 1$). Lakes with $E:I$ values > 1 are losing lake volume. Using those definitions, our survey of lakes found 66.1% of lakes within the U.S. were flow-though lakes, 33.6% were restricted-basin lakes, and $< 0.3\%$ were closed basin. Although these proportions shift slightly depending on the method used to predict δ_I, all three methods predict that $> 60\%$ of lakes are flow-through, and the restricted flow category varies around 35% of lakes for the summer of 2007. One reason for the high proportion of flow-through lakes was that 42% of lakes were man-made lakes and reservoirs, of which 80% were flow-through. For natural lakes, 54% were flow-though, and 45% had restricted flow. This difference in natural and man-made lakes could also be influencing our geographical distribution of $E:I$ because the southern half of the U.S. is dominated by man-made lakes (U.S. EPA 2009). Similar to our findings that $E:I$ varied with climatic region, Gibson and Edwards (2002) found $E:I$ differences between ecoclimatic regions of northern Canada, with the coldest tundra zone having the lowest $E:I$ values and the warmer boreal forest region having the highest. Within the U.S., although temperature was an important factor, it was not as important as was aridity, with relative humidity and annual precipitation being better predictors of $E:I$ and $\tau_{E:I}$ variation than temperature. The correlation of $E:I$ with relative humidity and precipitation was quite logical because these were the major drivers of evaporation and inflow to a lake.

Lake depth was the most important lake characteristic that related to variation in $E:I$ and $\tau_{E:I}$ (Fig. 6), followed closely by the volume of precipitation that falls within a lake's watershed. We are not aware of other studies that report on the influence of lake depth on $E:I$, but Noges (2009) found that τ and depth were positively correlated for European lakes. It does seem logical that lake depth would have a strong influence on these parameters, particularly for residence time, because lake volume was included in the calculation (Eq. 8) and lake depth was a parameter used to estimate volume (Hollister and Milstead 2010). Shallow lakes have shorter residence times and greater evaporation compared with deeper lakes (Fig. 6). We were surprised that lake area and lake volume were not better associated with $E:I$ and that depth was a better predictor than lake volume per unit area, although they were closely correlated. Lake area and depth were similarly important for $\tau_{E:I}$. The observation that deep lakes had the lowest level of $E:I$ indicated that lake stratification might not have had a large affect on water isotope values, even though the water samples were collected as a composite of the upper 2 m at the deepest point in the lake. Stratification would tend to concentrate the water enriched through evaporation in the epilimnion and thus overestimate $E:I$ relative to nonstratified lakes. We found that 85% of lakes deeper than 10 m were flow-through lakes ($E:I < 0.4$), whereas for lakes shallower than 2 m, only 40% were flow-through. Precipitation volume is negatively correlated with both $E:I$ and $\tau_{E:I}$ because it is closely related to lake inflow (I), which is in the denominator of both variables.

Total nitrogen (TN, mg L^{-1}) has been found to have a high relative risk to lake biological condition (U.S. EPA 2009; Van Sickle 2013), so hydrologic mechanisms that alter TN concentration within lakes would be of interest to the U.S. EPA. We found a strong positive correlation between lake $E:I$ and TN (Fig. 8), which was as strong as fertilizer loading within the watershed for explaining variation in lake TN. $E:I$ integrates many important

climate drivers, such as precipitation and evaporation, and hydrological processes, such as catchment runoff, groundwater inflows, and lake discharge, all of which can influence the biological activity and geochemical processes that can occur within the lake to alter the concentrations of biologically active dissolved solutes like carbon, nitrogen, and phosphorus (Fraterrigo and Downing 2008). Changes in hydrological cycling that drive $E:I$ can have profound effects on lake carbon budget (Cardille et al. 2009) and likely nitrogen budgets (Jeppesen et al. 2011). Changes in the proportion of lake inflow that leaves as evaporation indicate not only evaporative effects of concentrating solutes, but also reflect lake energy balances that would influence internal processing of biologically active nutrients. We found total phosphorus and Chl *a* were also correlated with $E:I$ (Table 2). Other studies have also found a close relationship between evaporation and water chemistry in lakes (Wolfe et al. 2007; Pham et al. 2008; Sokal et al. 2008). Yuan et al. (2011) found evaporation, as indicated by *d-excess*, was strongly correlated to total dissolved solutes in lakes from the Tibetan Plateau ($r = -0.69$), although in our study, *d-excess* was not as powerful a predictor as $E:I$ for lakes in the U.S. Pham et al (2008) also found evaporation to be a strong driver of solutes in lakes in the northern Great Plains of Canada. Wolfe et al. (2007) found that flow-through lakes had lower concentrations of a wide range of solutes including TN, dissolved organic carbon, and phosphorus. It is also possible that nutrient inputs via groundwater exchange may be more important in lakes with a high degree of closure, which might explain the increase in TN with $E:I$, although this remains to be investigated. Although more research should be done to determine exact linkages, our results clearly indicate that $E:I$ does indicate processes that influence lake nitrogen concentrations (Fig. 8).

Both estimates of τ were negatively correlated with lake chemistry (Table 2), but the correlations were not as strong as they were with $E:I$. (Table 2). Other studies have found residence time to be an important factor controlling lake chemistry (Noges 2009; Koiv et al. 2011; Finlay et al. 2013). The negative correlation with nutrient concentrations is expected, arising from the increase in retention rates associated with longer residence times, as observed in several other studies (Kaste et al. 2003; Harrison et al. 2009). Total phosphorus concentration was also found to be negatively correlated with hydraulic residence time (Brett and Benjamin 2008). Because lake hydrologic processes can either raise (i.e., by increasing $E:I$) or lower (i.e., through longer residence times) nutrient concentrations, they should be considered carefully when evaluating potential causes for elevated lake nutrient levels.

Our results indicate $E:I$ behaved similarly to chemical and physical stressors, at least in its relationship to lake biological condition. We found that lakes in poor biological condition had greater $E:I$ values than lakes in good biological condition (Fig. 9). The NLA used an index of phytoplankton and zooplankton taxon loss (O : E) as its primary biological indicator for determining lake condition (U.S. EPA 2009), and hydrological controls have often been linked with plankton assemblages and functional groups (Becker et al. 2010; Xiao et al. 2011; Rigosi and Rueda 2012). This link between biological condition and $E:I$ could be through the water chemistry connection described above or directly related to water mixing and flow-through, but because the two factors covary, it would be difficult to separate in the NLA (Van Sickle 2013). Factors such as lake depth, outflow regime, and lake mixing have all been directly related to plankton assemblages (Becker et al. 2010; Xiao et al. 2011; Rigosi and Rueda 2012) and were all related to $E:I$ within a lake. While we found weak correlations between residence time and indicators of biological condition (Table 2), others have found links between residence time and bacterial contaminants that influence human health (Romo et al. 2013) and that were used as recreation indicators within the NLA. For example, Romo et al (2013) noted that longer water residence times caused by dryer conditions were associated with increased toxic cyanobacteria biomass. Thus, lake hydrological parameters can be helpful in understanding the causes behind poor biological condition and water quality in lakes.

Lake hydrologic processes are fundamental in understanding lake biogeochemical cycling and the biological condition in lakes (Sokal et al. 2008; Tranvik et al. 2009; Becker et al. 2010). Our study indicated that $E:I$ values estimated from water isotope ratios determined on a single representative water sample collected from each lake were very useful indicators of hydrological condition for lakes evaluated in the 2007 NLA and were related to both nutrient concentrations and biological condition. The derived values of $E:I$ were more clearly correlated with lake chemistry and biological condition than were the parent isotope values from which they were derived, and $E:I$ values are more easily interpreted in a hydrologic sense, justifying the need for quantitative modeling used to derive $E:I$. Using the NLA survey design, these results have been scaled to represent the entire inference population of 50,000 lakes included in the 2007 NLA, thus representing the largest survey of $E:I$ and $\tau_{E:I}$ ever conducted. Our results illustrate that $E:I$ and $\tau_{E:I}$ modeling based on isotopic composition provide an excellent tool for approximating those hydrological characteristics across a wide range of lake and reservoir types and climate settings.

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