Ecological Tracers Can Quantify Food Web Structure and Change

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Disruption of natural food webs is becoming a commonplace occurrence as a result of human activities. Considering this, there is a need to improve our ability to define food web structure as well as to detect and understand the implications of trophodynamic change. This requires the development, validation, and application of ecological tracers that can provide insights into the movement of energy, nutrients, and contaminants through food webs. In this study, we examine the utility of two groups of naturally occurring intrinsic tracers (stable nitrogen isotopes and fatty acids) to provide such information in a predatory seabird, the herring gull (*Larus argentatus*). Spatial and temporal patterns in gull trophic position (inferred from egg stable nitrogen isotope values) were related to gull diet composition (inferred from egg fatty acid concentrations). These two independent groups of ecological tracers provided corroborating evidence that gull trophic position was related to the degree to which aquatic foods, namely fish, were consumed. The use of these tracers in concert led to a better understanding of routes of energy flow and contaminant transfer in food webs and how these pathways may be affected by ecosystem change.

Introduction

Humans are impacting the Earth's ecosystems to an unprecedented degree. Through the exploitation of natural resources, many species are being eliminated or decimated (*1*). As a result of international trade, exotic species have been transplanted across the globe, potentially leading to the homogenization of biotic communities (*2*). At the same time, the Earth's climate is being modified such that future distributions and relative abundances of species will be much different than today (*3*). Anthropogenic and natural factors are important in altering biological communities; however, such alterations often go unnoticed. There is a growing need to develop tools to improve our ability to recognize environmental change. One such need centers on improving our understanding of food web structure and how food webs may change through time. Food web structure is important in determining the flow of energy, nutrients, and contaminants through ecosystems.

Changes in food web structure over long periods may be difficult to detect, particularly if reliable historical data are not available. One way to address this problem is by examining alterations in food web trophodynamics. Trophodynamics describes predator−prey interactions while considering how these interactions may be affected by the biological, chemical, physical, and geological environment. High trophic level species can provide useful insights into trophodynamic change because they act as integrators of processes which, at lower trophic levels, alter prey species abundance and/or consumption. Insights into food web dynamics can be gained by analyzing ecological tracers in archived samples from integrator species. We define ecological tracers as stable chemical or biochemical compounds that can be used to understand the flow of energy and nutrients through food webs. Examples of ecological tracers include, but are not limited to, stable isotopes, fatty acids, amino acids, chemical elements, and organic pollutants.

In this paper, we examine how ecological tracers can provide insights into spatial differences and temporal changes in the trophodynamics of an integrator species within the Laurentian Great Lakes. The integrator species chosen for study was the herring gull (*Larus argentatus*). This species has been used to monitor environmental conditions in the Great Lakes since the early 1970s (*4*, *5*). A unique aspect of this program is that annual egg collections have been archived since its initiation. Thus, historic whole egg specimens were available for ecological tracer analysis. The chemical composition of these eggs would be expected to broadly reflect the diet of herring gulls during the period of egg formation. Biological communities among the Great Lakes differ, reflecting the physical and chemical characteristics of each lake along with each lake's unique biological history and evolution. In addition, biological communities on the Great Lakes have changed greatly over time. Fishing, habitat loss, nutrient inputs, and exotic species introductions have been important factors contributing to these changes (*6*). Lake Erie has undergone particularly profound change (*7*). In recent decades, the introduction of dreissenid mussels (*Dreissena polymorpha* and *D. bugensis*) has greatly altered nutrient dynamics and the composition of lower trophic level communities (*8*−*10*). For these reasons, the Great Lakes offer an excellent opportunity to investigate the utility of ecological tracers as indicators of food web structure and change. Here we discuss results stemming from the analysis of two types of naturally occurring intrinsic tracers, stable nitrogen isotopes, and fatty acids in herring gull eggs. Stable nitrogen isotopes were used to estimate herring gull trophic position, and fatty acids provided specific information regarding the type of foods herring gulls were consuming.

Stable nitrogen isotopes ($^{15}N/^{14}N$) have been used extensively in ecology for more than a decade (*11*). They have most frequently been used to estimate an organism's trophic position. They are useful in this regard because the $^{15}N/^{14}N$ ratio increases in a predictable fashion from one trophic level to the next (*12*, *13*). This has also been found to apply to avian eggs (*14*) where $\delta^{15}N$ ($(^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard} - 1) \times 1000$) values in egg protein were found to be 3.4‰ greater than those in the laying female's diet.

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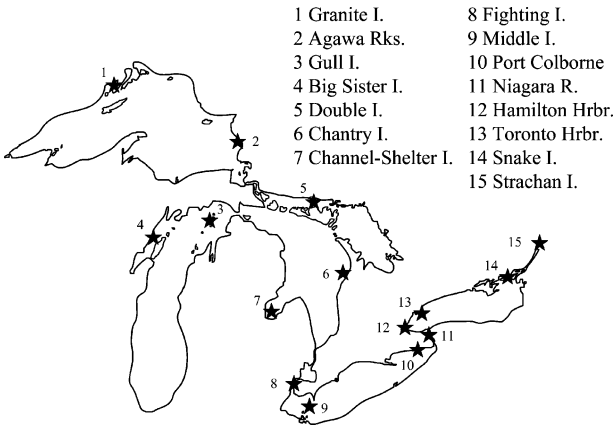

FIGURE 1. Location of herring gull monitoring colonies.

Fatty acids have been used less frequently as tracers of ecological processes; however, their use as tracers is rapidly increasing (*15*). They have been used to characterize diet composition of fish (*16*), marine mammals (*17*, *18*), and to a lesser extent, birds (*19*). Here, we further showcase the usefulness of fatty acid data in an ecological tracer context.

Fatty acids are required for normal growth and development; however, some fatty acids either cannot be synthesized at all or cannot be synthesized with high efficiency in higher trophic level organisms. Instead, these long carbon-chain, "essential" fatty acids are formed by primary producers and are passed up the food chain through consumption. During such trophic transfers, the fatty acid signatures of prey are largely retained in higher trophic level species (*18*, *20*). The degree to which fatty acid profiles in the diet are reflected in consumers has been demonstrated in a variety of consumer tissues including eggs. For example, in laboratory feeding trials, laying chickens were fed different amounts of omega 3 (n-3) polyunsaturated fatty acids (PUFAs) (*21*). Omega-3 PUFAs are characterized by the first double bond occurring on the third carbon from the methyl end of the molecule's hydrocarbon chain and include such fatty acids as eicosapentaenoic acid (EPA, C20:5n-3), docosapentaenoic acid (DPA, C22:5n-3), and docosahexaenoic acid (DHA, C22:6n-3). Hens fed diets containing more n-3 PUFAs laid eggs containing more EPA and DPA (*21*). The conservation of fatty acid profiles during trophic transfer is one of the reasons why these compounds have such potential as ecological tracers. In addition, the fatty acid compositions of various food/prey types differ (*22*, *23*). For example, there are differences in the fatty acid composition of aquatic and terrestrial organisms. In general, aquatic organisms such as fish contain greater amounts of the n-3 PUFAs, e.g., EPA. In terrestrial organisms, n-6 PUFAs are relatively more abundant. Thus, the ratio of n-3 to n-6 PUFAs can be a useful indicator of the amount of aquatic versus terrestrial food in an organism's diet (*22*, *23*).

Using the concepts summarized above, stable isotope and fatty acid patterns in herring gull eggs were used to investigate the following: (1) Spatial differences in Great Lakes food web structure. We hypothesized that by using ecological tracers we would be able to identify differences in herring gull trophodynamics on each of the Great Lakes. (2) We hypothesized that temporal changes in ecological tracer patterns in herring gull eggs would be apparent, and that these changes could provide insights into changes in the food webs of Lake Erie. Eastern Lake Erie was the focus because of previously reported changes in herring gull stable isotope data from that lake (*24*) and because of documented changes in ecosystem structure (*8*−*10*).

TABLE 1. Inter-colony Differences in Mean Values of Endpoints Measured in Herring Gull Eggs Collected in 1982, 1987, 1992, 1997, and 2004.[a]

colony	waterbody	TP	n-3/n-6	EPA	DPA	n-3
1. Granite	Superior	3.54^{abc}	0.65^{a}	1.71^{abc}	1.28^{ab}	14.92^{a}
2. Agawa	Superior	3.60^{abc}	0.58^{ab}	1.43^{abcd}	1.29^{ab}	14.41^{a}
3. Gull	Michigan	3.76^{abc}	0.69^{a}	2.17^{a}	1.83^{a}	17.40^{a}
4. Big Sister	Michigan	3.91^{abc}	0.61^{ab}	1.63^{abc}	1.41^{ab}	14.23^{a}
5. Double	Huron	3.76^{abc}	0.58^{ab}	1.52^{abcd}	1.50^{ab}	15.84^{a}
6. Chantry	Huron	3.35^{abc}	0.50^{ab}	1.16^{bcd}	1.27^{ab}	13.01^{a}
7. Channel-Shelter	Huron	3.49^{abc}	0.57^{ab}	1.46^{abcd}	1.46^{ab}	15.17^{a}
8. Fighting	Detroit River	3.19^{c}	0.57^{ab}	1.13^{bcd}	1.67^{ab}	15.17^{a}
9. Middle	Erie	4.21^{a}	0.69^{a}	1.87^{abc}	1.90^{a}	15.42^{a}
10. Port Colborne	Erie	3.92^{abc}	0.58^{ab}	1.83^{abc}	1.29^{ab}	15.91^{a}
11. Niagara	Niagara River	4.07^{ab}	0.68^{a}	1.97^{ab}	1.22^{ab}	14.71^{a}
12. Hamilton	Ontario	3.14^{c}	0.59^{ab}	1.59^{abcd}	1.31^{ab}	14.75^{a}
13. Toronto	Ontario	3.28^{bc}	0.49^{ab}	0.97^{cd}	0.94^{b}	12.05^{a}
14. Snake	Ontario	3.14^{c}	0.52^{ab}	1.16^{bcd}	1.01^{b}	13.14^{a}
15. Strachan	St. Lawrence River	3.22^{abc}	0.41^{c}	0.56^{d}	0.95^{b}	11.75^{a}

[a] Significant differences (Tukey's HSD test) in trophic position (TP), Omega 3 to Omega 6 fatty acid ratios (n-3/n-6), eicosapentaenoic acid (EPA), docosapentaenoic acid (DPA), and total Omega 3 fatty acids (n-3) are indicated by superscript letters. Colonies with the same letter are not significantly different.

Materials and Methods

Egg Collection, Storage, and Analysis. Details regarding egg collections are given elsewhere (*4*). Briefly, 13 herring gull eggs were collected annually at each of 15 colonies on the Great Lakes as part of Environment Canada's Great Lakes Herring Gull Monitoring Program (GLHGMP) (Figure 1). For each year at each colony, these samples were pooled on an equal weight basis. Subsamples of whole egg homogenate pools were stored at −40 °C (1974−2004) and at −80 °C (1982−1997) at the time of initial collection.

Stable Nitrogen Isotope and Fatty Acid Analysis. Protocols for stable nitrogen isotope analysis have been reported previously (*25*). Fatty acid methyl esters (FAME) were obtained in a three-step process: extraction, derivatization, and quantification on a gas chromatograph (GC). Samples were extracted three times by grinding freeze-dried tissue in (2:1 vol:vol) chloroform:methanol (*26*) and centrifuged at 4000 rpm to remove nonlipid material. From a final volume of 2 mL, duplicate, 200 μL aliquots were dispensed into preweighed vessels which were dried and re-weighed on a Sartorius M5 electron balance with 1 μg precision to provide a quantitative measure of total lipid content. The remaining extract (1.6 mL) was then transferred into a 5 mL Shimadzu vial (Sigma no. 27319U) and evaporated to dryness using nitrogen gas and stored at −80 °C until derivatization.

The FA extracts were resuspended in 2 mL hexane prior to derivitization. Two ml of BF3-methanol (10% w/w) was added and vials were heated (70 °C) for 2 h, after which 1 mL each of water was added. The FAME-containing hexane-layer was carefully removed and placed into a 2 mL Kuderna−Danish receiving vial (Sigma no. 6−4689U). One mL hexane was then added to the original Shimadzu vial to extract the remaining FAME. This step was repeated once more to get the best extraction efficiency (90−95%).The FAME−hexane solution was evaporated to 2.0 mL using nitrogen gas and transferred to a 2 mL glass GC vial and stored in a −80 °C cryogenic freezer prior to GC analysis.

FAME concentrations were quantified on a Hewlett-Packard 6890 GC with the following configuration: splitless injection; column: Supelco (SP-2560 column) 100 m × 0.25 mm i.d. × 0.20 μm thick film; Oven: 140 °C (hold 5 min) to 240 °C at 4 °C/min, hold for 12 min; helium carrier gas, 1.2 mL/min; flame ionization detector at 260 °C; injector at 260

°C; total run time = 42 min/sample. A 37-component FAME standard (Supelco no. 47885-U) was used to identity and quantify (4-point calibration curves) FAME in the samples (unknowns) i.e., by comparing their retention times to those of the FAME standard. Results are reported as μg FAME/mg dry weight tissue.

PUFAs are prone to oxidation (*27*) and could, therefore, potentially be lost during storage at temperatures warmer than −80 °C. To investigate the possibility that PUFAs might be lost during storage at −40 °C, a comparative analysis was undertaken examining PUFA levels in a set of samples that was split and stored at both −40°C and −80°C at the time of initial archiving. Annual pooled samples included in this analysis were from Port Colborne, eastern Lake Erie, 1982−1997.

Using Ecological Tracers to Define Food Web Structure. Stable nitrogen isotopes and fatty acids were measured in herring gull egg pools from each of the 15 GLHGMP colonies during 1982, 1987, 1992, 1997, and 2004. All of these samples had been stored at −80 °C except for the 2004 samples which were stored at −40 °C. Mean values were calculated using data from these years to provide an average assessment of trophodynamic interactions at each colony during the 1982−2004 period.

Because of inter-lake differences in baseline δ^{15}N signatures (see *24*) it was not valid to compare raw δ^{15}N egg values among lakes. Instead, egg δ^{15}N values were used to provide an estimate of gull trophic position that accounted for baseline differences. Procedures to calculate gull trophic position are described elsewhere (*24*). Briefly, trophic position (TP) was calculated using the following equation:

$$TP = [(\delta^{15}N_{gull} - \delta^{15}N_{fish})/3.4] + 3$$

$\delta^{15}N_{fish}$ values were lake-specific and identical to those described previously (*24*) with one exception. Trophic position estimates for the Channel Shelter Island colony in Saginaw Bay, Lake Huron were revised to make use of Saginaw Bay specific fish isotope data ($\delta^{15}N_{smelt}$ = 13.24‰; Brian Eadie, NOAA, personal communication). The $\delta^{15}N_{fish}$ values for each lake were based upon the isotopic signatures of the fish species that were the main prey species for herring gulls in that lake (see ref *24* for details). These estimates of trophic position were compared across lakes and colonies. ANOVA and Tukey's honestly significant difference test were used to compare trophic position and fatty acid data among colonies (*28*). Linear regressions were used to examine the factors contributing to spatial differences in food web structure (*28*). In all tests, $p < 0.05$ was deemed to be significant.

Using Ecological Tracers to Detect Food Web Change. Annual pooled egg samples from Port Colborne, eastern Lake Erie, 1980−2004, were analyzed for stable nitrogen isotopes and fatty acids. Linear regressions were used to examine the factors contributing to temporal changes in food web structure in Lake Erie (*28*). Statistical tests were deemed significant at $p < 0.05$.

Results and Discussion

Effect of Storage Conditions on Egg Fatty Acid Levels. There were no significant differences in levels of EPA, DPA, DHA, total n-3, total n-6, total saturated fatty acids, total monounsaturated fatty acids, or total PUFAs between split samples stored at −40 °C versus −80 °C (t-tests, $p > 0.35$). These results provide preliminary evidence that samples stored at −40 °C are appropriate for fatty acid analysis.

Using Ecological Tracers to Define Food Web Structure. There were significant differences in trophic position estimates for herring gulls breeding on the Great Lakes (ANOVA, $F_{14,59} = 4.04$, $p < 0.001$). Mean trophic position estimates for individual colonies ranged from 3.14 at Snake Island/Hamilton Harbour in Lake Ontario to 4.21 at Middle Island in Lake Erie (Table 1). Estimates of herring gull trophic position indicated that gulls from different colonies were feeding on prey occupying different trophic positions. Fatty acid analyses of the same samples indicated that there were differences among colonies in egg fatty acid patterns. There were significant differences among colonies in n-3/n-6 fatty acid ratios (ANOVA, $F_{14,59} = 3.55$, $p < 0.001$) and in levels of the individual fatty acids EPA (ANOVA, $F_{14,59} = 3.78$, $p < 0.001$) and DPA (ANOVA, $F_{14,59} = 3.68$, $p < 0.001$). Total n-3 fatty acids showed nonsignificant inter-colony differences (ANOVA, $F_{14,59} = 1.78$, $p = 0.06$). There were no significant inter-colony differences in n-6, total saturated, total monounsaturated, or total polyunsaturated fatty acids (ANOVA, $p > 0.30$ in all cases).

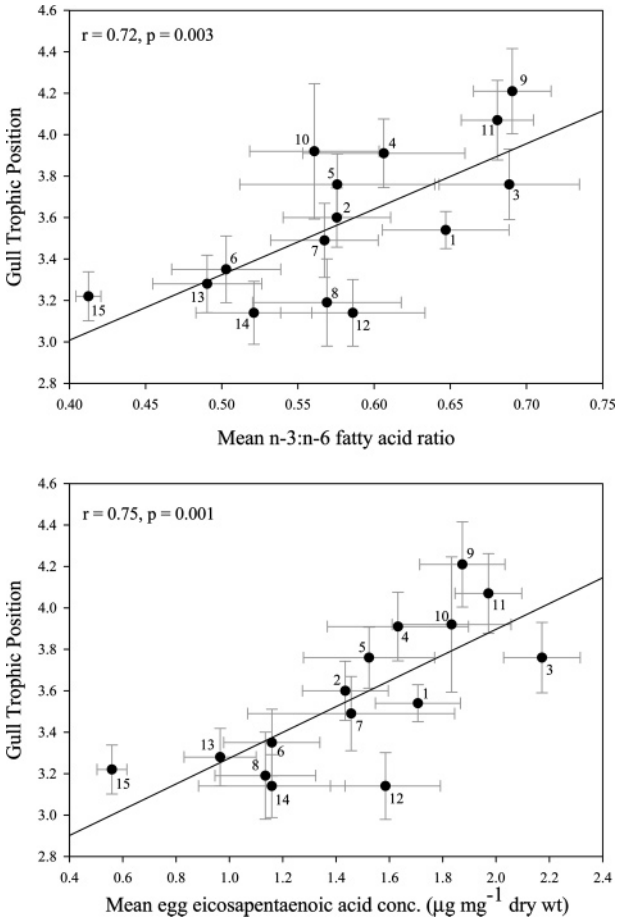

FIGURE 2. (a) Relationship between mean trophic position and mean ratio of Omega 3 (n-3) to Omega 6 (n-6) fatty acids in gull eggs, (b) Relationship between mean trophic position and mean concentration of eicosapentaenoic acid (EPA) in gull eggs. Mean (±1 standard error) values were calculated for each of 15 monitoring colonies using annual data from 1982, 1987, 1992, 1997, and 2004. Numbers beside each point refer to the colonies indicated in Figure 1.

Estimates of gull trophic position and egg n-3/n-6 fatty acid ratios were correlated (Figure 2a). Gull trophic position was also correlated with EPA (Figure 2b) and total n-3 fatty acid concentrations in eggs ($r = 0.54$, $p = 0.04$). Egg DPA concentrations and trophic position were not significantly correlated ($r = 0.50$, $p = 0.06$).

These results indicated that inter-colony differences in trophic position were likely the result of birds at different colonies feeding to differential degrees on aquatic versus terrestrial foods. As the amount of aquatic food in the gull diet increased (as inferred from n-3/n-6 fatty acid ratios) the trophic position of the birds also increased. Fish occupy

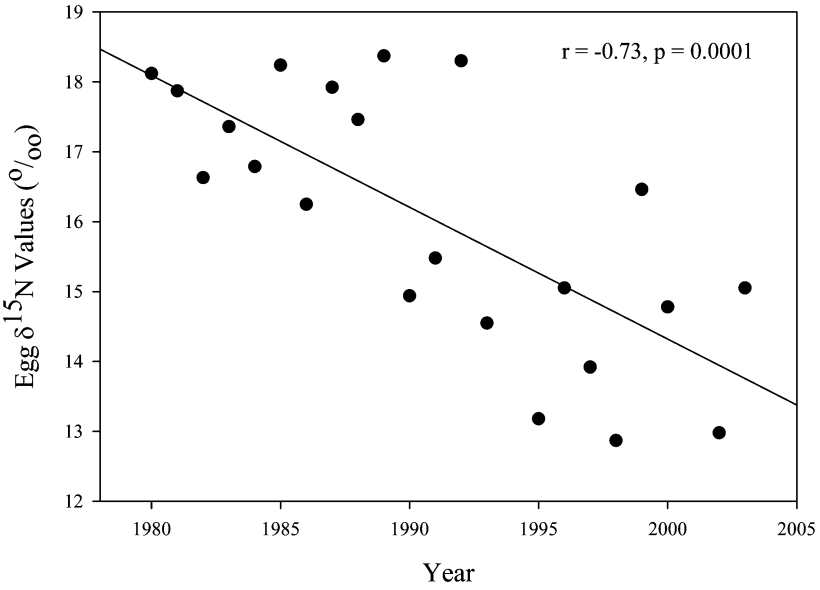

FIGURE 3. Temporal trends in egg δ^{15}N values from Port Colborne, eastern Lake Erie.

higher trophic levels than most other prey that gulls consume (*24*, *25*, *29*). Further insights into how differences in diet lead to differences in trophic position were obtained by examining levels of individual fatty acids associated with particular food types. Omega-3 fatty acids, e.g., EPA, are found in high concentrations in fish especially oily fish such as smelt (*30*). Eggs containing greater concentrations of these fatty acids likely reflected greater fish consumption at those colonies. Through the use of stable nitrogen isotopes and fatty acid tracers we have gained further insights into the degree to which aquatic foods, namely fish, are important in the diets of Great Lakes herring gulls. Inter-colony differences in fish consumption likely reflect regional differences in fish availability manifested through differences in primary production and other factors (*29*, *31*). The degree to which fish are consumed is likely the primary factor regulating the trophic position of herring gulls within the Great Lakes. This allows us to use changes in herring gull trophic position (as inferred from δ^{15}N values) and fatty acid composition as indicators of alterations in prey fish availability and pathways of energy flow in food webs.

Using Ecological Tracers to Detect Food Web Change. Previous research demonstrated a significant positive relationship between annual estimates of prey fish abundance and egg δ^{15}N values in eastern Lake Erie (*25*). Temporal changes in the Lake Erie ecosystem that have resulted in declines in prey fish availability are likely responsible for reductions in the amount of fish being consumed by herring gulls in eastern Lake Erie. Fish generally are a high quality food rich in nutrients and energy (*32*). The ramifications to breeding herring gulls of relying on other prey types of lower nutritional quality are known from other parts of the Great Lakes (*31*). In areas where gulls rely less on fish, they are in poorer condition and reproductive success is lower (*31*).

In this study, there was a temporal decline in egg δ^{15}N values from eastern Lake Erie ($r = -0.73$, $p = 0.0001$) (Figure 3). We interpret this decline as an indication of a reduction in herring gull trophic position. Another possible explanation is that there has been a decline in δ^{15}N values at the base of the food web. Such a baseline change could occur as a result of alterations in the relative importance of different nitrogen sources entering the lake. If baseline changes were responsible for the decline in herring gull egg δ^{15}N values we would expect that similar δ^{15}N trends would be evident in other biomonitoring species. Contrary to this expectation, δ^{15}N values in Lake Erie walleye (1978−1995) (*33*) and double-crested cormorant eggs (1981−1995) (C. E. Hebert, unpublished data) show no temporal decline. Clearly, further research is needed to examine this issue, but based upon available data, we believe that changes in food web dynamics were the most likely cause of declines in herring gull egg δ^{15}N values.

Results of the fatty acid analyses provided support for the above interpretation of the stable nitrogen isotope data. Egg δ^{15}N values were positively correlated with egg concentrations of EPA ($r = 0.72$, $p = 0.0001$) (Figure 4), DPA ($r = 0.50$, $p = 0.02$), DHA ($r = 0.47$, $p = 0.03$) and total n-3 fatty acids ($r = 0.59$, $p = 0.01$). The n-3/n-6 fatty acid ratio was also positively correlated with egg δ^{15}N values ($r = 0.74$, $p = 0.0001$) (Figure 5). There were no correlations between egg δ^{15}N values and concentrations of total n-6, total saturated, total monounsaturated, or total PUFA concentrations. These results indicate that, in years when gulls appeared to have fed to a greater extent on aquatic prey (i.e., fish), their trophic position, as measured using stable nitrogen isotopes, was higher. These changes in trophic position were correlated with changes in diet composition. In years when more aquatic food appeared to be consumed gull trophic position was greater. Thus, the application of ecological tracers provided the means to quantitatively assess changes in diet composition, and the results presented here provide the first quantitative evidence linking dietary shifts to temporal declines in gull trophic position.

In Lake Erie, introduced dreissenid mussels may have contributed to declines in pelagic prey fish abundance (*34*). The redirection of primary production from the pelagic zone of the lake to the benthos may have reduced the carrying capacity of the lake for pelagic prey fish such as the rainbow smelt (*Osmerus mordax*) and emerald shiner (*Notropis atherinoides*). Surface-feeding herring gulls are reliant on such pelagic fish as important components of their diet (*35*). The resulting impacts on food web structure in eastern Lake Erie are producing detectable changes in our integrator species, the herring gull. Continued surveillance of herring gulls on Lake Erie and in other locations where declines in trophic position may be observed is required to determine whether shifts in fish consumption as a result of food web change will result in the reduced fitness of individual gulls with concomitant declines in breeding success and, perhaps, populations.

The results reported here highlight the usefulness of ecological tracers in understanding pathways of energy flow

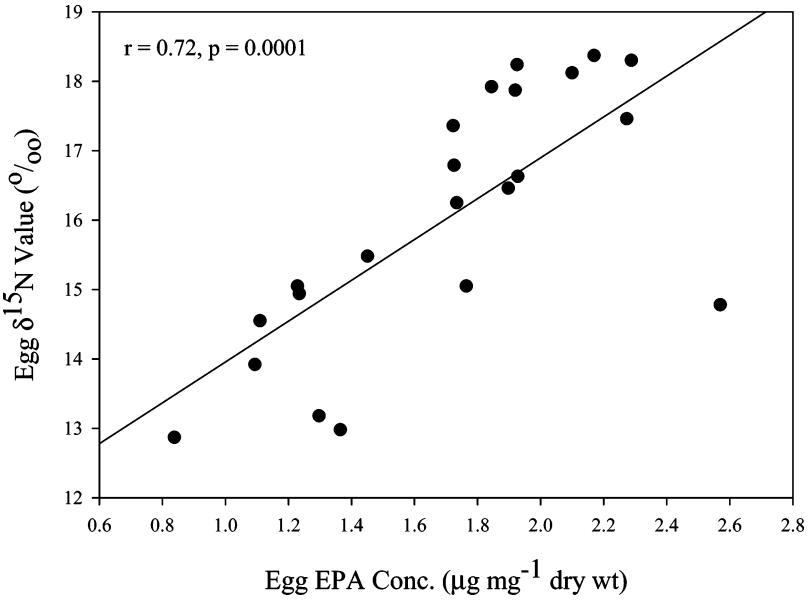

FIGURE 4. Relationship between egg eicosapentaenoic acid (EPA) concentrations and egg δ^{15}N values. EPA concentrations are greater in aquatic foods, particularly fish. Higher δ^{15}N values imply gulls were feeding at higher trophic levels.

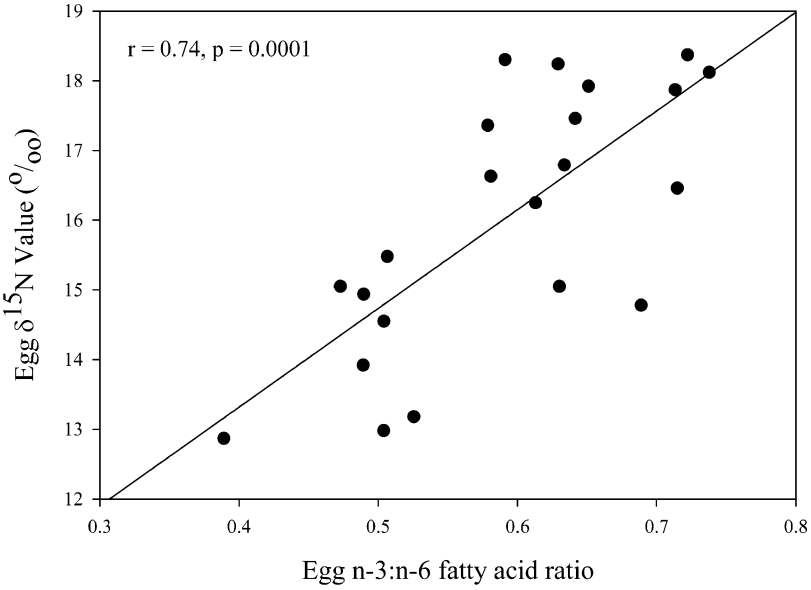

FIGURE 5. Relationship between egg n-3/n-6 fatty acid ratios and egg δ^{15}N values. Higher n-3/n-6 fatty acid ratios are found in aquatic foods.

to high trophic levels. In this study, stable nitrogen isotopes (δ^{15}N) provided the means to assess spatial differences and temporal changes in species trophic position. In that context, results of this study are similar to others (*11*). However, the addition of fatty acid tracers provided insights into the food web changes that influenced species trophic position. These insights would not have been possible using δ^{15}N data alone. In addition, in our study, the interpretation of the fatty acid dietary signatures was quite rudimentary (e.g., aquatic versus terrestrial foods). With additional research to characterize the fatty acid composition of food web components, it might be possible to estimate the relative contribution of individual prey species/food types to the diets of higher trophic level predators (see ref *18*). However, for such analyses to be informative, further research is required to determine the degree to which predator metabolic processes will cause fatty acid profiles in predator and prey to diverge (*36*).

Understanding the processes regulating diet composition in integrator species will improve our ability to use other complimentary data from such species to gain better insights into how large-scale changes affect the ecosystem. Use of indicator species to evaluate environmental quality requires a sound understanding of the factors that affect what that species is integrating. For example, the herring gull has been used to monitor levels and effects of contaminants on the Great Lakes for decades. Correct interpretation of temporal trends in biomagnifying contaminants requires an understanding of how food web processes have changed through time. Changes in trophic position as a result of food web change need to be considered if we are to use such data to accurately evaluate progress in reducing the bioavailability of persistent, lipophilic contaminants in the Great Lakes (see ref *37*). Through the development, validation, and application of ecological tracers such as stable nitrogen isotopes and fatty acids, the utility of environmental monitoring data will be enhanced.

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