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PHYSIOLOGICAL ECOLOGY - ORIGINAL PAPER

Biochemical tracers reveal intra-specific differences in the food webs utilized by individual seabirds

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Abstract Food web structure regulates the pathways and flow rates of energy, nutrients, and contaminants to top predators. Ecologically and physiologically meaningful biochemical tracers provide a means to characterize and quantify these transfers within food webs. In this study, changes in the ratios of stable N isotopes (e.g., δ^{15}N), fatty acids (FA), and persistent contaminants were used to trace food web pathways utilized by herring gulls (*Larus argentatus*) breeding along the shores of the St Lawrence River, Canada. Egg δ^{15}N values varied significantly among years and were used as an indicator of gull trophic position. Temporal trends in egg δ^{15}N values were related to egg FA profiles. In years when egg δ^{15}N values were greater, egg FA patterns reflected the consumption of more aquatic prey. Egg δ^{15}N values were also correlated with annual estimates of prey fish abundance. These results indicated that temporal changes in aquatic prey availability were reflected in the gull diet (as inferred from ecological tracer profiles in gull eggs). Analysis of individual eggs within years confirmed that birds consuming more aquatic prey occupied higher trophic positions. Furthermore, increases in trophic position were associated with increased concentrations of most persistent organic contaminants in eggs. However, levels of highly brominated polybrominated diphenyl ether congeners, e.g, 2,2′,3,3′,4,4′,5,5′,6,6′-decabromoDE (BDE-209), showed a negative relationship with trophic position. These contrasting findings reflected differences among contaminant groups/homologs in terms of their predominant routes of transfer, i.e., aquatic versus terrestrial food webs. High trophic level omnivores, e.g., herring gulls, are common in food webs. By characterizing ecological tracer profiles in such species we can better understand spatial, temporal, and individual differences in pathways of contaminant, energy, and nutrient flow.

Keywords Stable nitrogen isotopes · Fatty acids · Persistent contaminants · St Lawrence River · Omnivores

Introduction

Diet composition plays a key role in regulating the flow of energy, nutrients, and contaminants to biota. Differences in the diets of individuals may be important in regulating their relative fitness (Metcalfe and Monaghan 2001). Traditional approaches to evaluate such differences have relied on intensive observations of prey provisioning (Gaston et al. 2003), detailed study of dietary remains, e.g., pellets (Ewins et al. 1994; Fox et al. 1990), or radio-tracking/satellite telemetry studies to define foraging areas and behaviors (Gorke and Brandl 1986; Morris and Black 1980; Wood et al. 2000). All of these methods have proven useful. However, another approach to gain insights into individual and/or population differences in foraging behavior and diet

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composition is by measuring intrinsic ecological tracers in consumer tissues (Hebert et al. 2006).

High trophic level predators act as integrators of food web processes (Hebert et al. 2006). However, because many "predators" can be, under certain circumstances, quite omnivorous (Thompson et al. 2007), individuals may track resource availability in different ways leading to differences in diet composition among individuals. Insights into these differences can be gained by analyzing ecological tracers in the tissues of such species. Ecological tracers are chemically or biochemically stable compounds within organisms and thus can be used to understand the flow of energy and nutrients through food webs. Examples of ecological tracers include: stable isotopes such as those of N and C, fatty acids (FA), biomagnifying pollutants, amino acids, and chemical elements (Hebert et al. 2006).

We used ecological tracers in herring gulls (*Larus argentatus*) from the upper St Lawrence River to examine temporal changes in the gull diet and elucidate dietary differences among individuals. The chemical composition of these eggs reflects the diet of herring gulls during the period of egg formation (Hobson et al. 1997) and thus eggs from this species have been used to monitor environmental conditions in the Laurentian Great Lakes, St Lawrence River, Atlantic Canada, and Europe for decades (Elliott et al. 1992; Gilbertson 1974; Hebert et al. 1999a; Mineau et al. 1984; Oxynos et al. 1993; Marth et al. 2000; Weseloh et al. 2006). Herring gulls on the Great Lakes are thought to be facultative piscivores, that is, when fish are available they are consumed preferentially; however, as fish availability declines gulls switch to other food resources (Ewins et al. 1994; Hebert et al. 1999b, 2008). Therefore, as is typical of many high trophic level species (Thompson et al. 2007), there is potential for significant variation in the herring gull diet.

The ecological tracers that are the focus of this study are stable N isotopes, FA, and biomagnifying contaminants. Stable N isotopes ($^{15}N/^{14}N$) are valuable indicators of organism trophic position (see Kelly 2000 for a review). 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 (Minagawa and Wada 1984; Peterson and Fry 1987). This also pertains to avian eggs where the stable N isotope ratio ($\delta^{15}N$) ($^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard} - 1$) values in egg protein were 3.4‰ greater than those in the food consumed by the egg-laying female (Hobson 1995).

The use of FA as tracers of food web processes is gaining acceptance in ecological and environmental studies (Dalsgaard et al. 2003). FA are the main constituents of many types of lipid and are required for normal growth and development. Some FA are designated "essential" because they cannot be efficiently synthesized by consumers; instead, they originate in primary producers (Arts et al. 2001). These FA are highly conserved during trophic interactions (Kainz et al. 2004) in aquatic food webs. Their utility as tracers of food web pathways stems from the fact that, during trophic transfer, prey FA patterns are to varying degrees retained in higher trophic level species, allowing inferences to be made regarding consumer diet composition (Napolitano 1998; Iverson et al. 2004). Furthermore, food types differ in their FA composition and these differences can, under some circumstances, provide insights into pathways of energy and nutrient transfer (Napolitano 1998, Iverson et al. 2004). For example, there are differences in the FA composition of terrestrial and aquatic organisms. In general, aquatic organisms contain greater amounts of omega 3 (n-3) polyunsaturated FA (PUFA), e.g., eicosapentaenoic acid (EPA; 20:5n-3), docosapentaenoic acid (DPA; 22:5n-3), and docosahexaenoic acid (DHA; 22:6n-3). Terrestrial organisms have a greater abundance of n-6 PUFA, e.g., linoleic acid (18:2n-6). Thus, the ratio of n-3 to n-6 PUFA can be a useful indicator of the amount of aquatic versus terrestrial food in an organism's diet (Skjervold 1992; Addis 2005; Koussoroplis et al. 2008).

Levels of persistent, biomagnifying contaminants in top predators, such as the herring gull, are primarily regulated by exposure and accumulation through the diet. Concentrations of biomagnifying contaminants generally increase with trophic level when comparing species across entire food webs (see Jardine et al. 2006). However, few studies have examined the relationship between trophic position and contaminant levels among individuals within a species in the wild (Bearhop et al. 2000; Nisbet et al. 2002). With respect to herring gulls, individuals incorporating more aquatic food in their diets would be expected to occupy higher trophic positions. This reflects the fact that species constituting their aquatic prey base occupy higher trophic positions than terrestrial food items (Hebert and Sprules 2002). Therefore, individual differences in trophic position could result from selection of aquatic versus terrestrial prey. This, in turn, could also affect exposure to, and accumulation of, biomagnifying contaminants (see Hebert et al. 2000). Here, we examine the degree to which three independent groups of ecological tracers (stable N isotopes, FA, and biomagnifying pollutants) can provide insights into pathways of energy and nutrient flow within one species, the herring gull. First, temporal changes in gull egg N isotopes and FA are examined relative to temporal changes in aquatic prey availability. Second, ecological tracer profiles in individual eggs from 2001/2002 are used to characterize dietary differences among individual birds.

Materials and methods

Egg collections

Annual herring gull egg collections (one egg from each of ten to 13 nests) were made at Strachan Island (45°02′ N, 074°82′ W) in Lake St Lawrence from 1986 to 2005 (except 1987). Lake St Lawrence is a man-made lake that resulted from upstream flooding due to the construction of the Moses-Saunders dam at Cornwall, Ontario in the 1950s. Strachan Island is located approximately 1 km upstream from the dam within the Cornwall/Massena Areas of Concern (AOC), two of 43 such polluted areas in the Great Lakes/St Lawrence River (International Joint Commission 1987). Radio telemetry studies of the feeding ecology of herring gulls along Great Lakes' connecting channels, i.e., Detroit River, indicate that they feed within 10 km, upstream and downstream, of the breeding colony (Canadian Wildlife Service, unpublished data). Therefore, the entire physical extent of the Cornwall/Massena AOC was within the daily feeding range of herring gulls from Strachan Island. However, as the gulls also feed upstream from the dam, their feeding range would include areas outside the AOC as well.

Tracer analysis

After collection, egg samples were individually homogenized and aliquots stored frozen at the National Wildlife Research Centre (NWRC). Individual and/or pooled samples were used for stable isotope (−40°C), contaminant (−40°C), and FA (−80°C) analyses. When required, pooled samples were created by combining tissues from different eggs on an equal weight basis for each year. The creation of pooled samples was, at times, necessary because of fiscal considerations.

Stable isotope values in individual eggs were measured in ten eggs annually throughout the 1986–2002 period (n = 170). Pooled samples were analyzed from 2003 to 2005. Exogenous resources are primarily used for egg formation in herring gulls; therefore, egg stable isotope values were expected to reflect the isotopic composition of the herring gull diet during the several-week period of egg formation (Hobson et al. 1997). Gulls arrive on their breeding colonies at least a month prior to egg-laying to initiate reproductive activities, e.g., territory establishment and defense, nest construction. Therefore, egg isotope values were expected to reflect environmental conditions at the breeding colony.

Stable isotope analyses were completed at the University of Saskatchewan. Protocols for stable N isotope analysis have been reported previously (Hebert et al. 2000). Briefly, 1 ml subsamples of individual eggs or pools were freeze-dried and lipids were removed using several 2:1 chloroform:methanol rinses. Stable N and C (not reported here) isotope analyses were conducted on these lipid-free subsamples. Approximately 1 mg of powdered sample was weighed into tin cups and combusted at 1,800°C in a Robo Prep elemental analyser interfaced with a Europa 20:20 continuous flow isotope ratio mass spectrometer. Samples were placed in a sequence of two laboratory standards (albumen) for every five unknowns. Results were expressed in delta (δ) notation, as parts per thousand (‰) deviation from a standard (air).

FA methyl esters (FAME) were measured in pooled egg samples collected from 1986 to 2005. In addition, for the years 2001 and 2002, ten individual eggs were analyzed from each year. FAME were measured in three steps: extraction, derivatization, and quantification. A total of 30–40 mg samples were extracted 3 times by grinding freeze-dried tissue in (2:1 vol:vol) chloroform:methanol (Bligh and Dyer 1959) and centrifuged at 4,000 r.p.m. to remove non-lipid material. From a final volume of 2 ml, duplicate, 200-µl aliquots were dispensed into pre-weighed 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 N gas and stored at −80°C until derivatization. The FA extracts were resuspended in 1.5 ml toluene prior to derivatization. Two milliliters of H_2SO_4/methanol (1%) were added to the tube before overnight methylation (16 h) in a water bath at 50°C. The extract was then evaporated to dryness under N, and redissolved in 2 ml hexane. A 250-µl portion of the resulting extracts was used for FAME analysis; remaining extract was archived at −80°C.

FAME concentrations were quantified using a capillary gas chromatograph (Agilent 6890N) coupled with a flame ionization detector. Instrument configuration was as follows: splitless injection; column = Supelco (SP-2560 column) 100 m × 0.25 mm internal diameter × 0.20-µm-thick film; oven = 140°C (hold 5 min) to 240°C at 4°C/min, hold for 12 min; He 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 identify and quantify (four-point calibration curves) FAME in the samples, i.e., by comparing their retention times to those of the FAME standard. Results were reported as microgram FAME per milligram dry weight tissue.

Ten individual eggs from each of 2001 and 2002 were analyzed for persistent contaminants [Hg, organochlorines, and polybrominated diphenyl ethers (PBDE)]. These years were chosen because they represented the most recent years for which individual stable isotope and FA data were available.

Total Hg analysis was conducted on the 2001/2002 eggs at the University of Windsor's Great Lakes Institute for Environmental Research according to GLIER (2008). Samples were thawed, freeze-dried, and digested in 2:1 H_2SO_4/HNO_3 prior to analysis. Hg analysis was completed using cold vapor atomic absorption spectrophotometry (CVAAS) with the 300-AAS (Varian) equipped with a vapor generation system. Analytical accuracy for total Hg was determined by analyzing one or two blank samples with each sample set, as well as analysis of standard reference materials (DOLT-2, DORM-1 from the Canadian National Research Council). Analytical precision was checked by analyzing replicate samples. Recovery of reference materials was within the certified range for all methodologies and nominal detection limits were 0.075 μg g^{-1} dry weight sample for total Hg.

Organochlorine contaminant analyses were also conducted at the University of Windsor's GLIER. Methods are described in Lazar et al. (1992). Organochlorine analyses included determination of 1,2,3,4- and 1,2,4,5-tetrachlorobenzene (TCB), pentachlorobenzene (QCB), hexachlorobenzene (HCB), α-, β- and γ-hexachlorocyclohexane (HCH), oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, heptachlor epoxide, dichlorodiphenyltrichloroethane (DDT), *p,p'*-dichlorodiphenyldichloroethylene (DDE), *p,p'*-dichlorodiphenyldichloroethane (DDD), octachlorostyrene (OCS), mirex, dieldrin, and polychlorinated biphenyl (PCB) congeners. ΣChlorobenzene (TCBs + QCB + HCB), Σchlordane (chlordanes + nonachlors + heptachlor epoxide), ΣDDT (DDT + DDE + DDD) were also calculated. ΣPCB consisted of 45 congeners identified according to IUPAC numbers (Ballschmiter et al. 1992) and included congener numbers 28, 31, 42, 44, 49, 52, 60, 64, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 118, 128, 138, 141, 146, 149, 151, 153, 158, 170, 171, 172, 174, 177, 178, 179, 180, 182, 183, 187, 190, 194, 195, 200, 201, 203, and 206. Congeners 66/95, 182/187, and 170/190 co-eluted and were reported together. The nominal detection limit was 0.1 ng g^{-1} wet weight.

PBDE were measured at NWRC according to methods described in (Gauthier et al. 2008). Nomenclature for PBDEs is the same as that for PCBs (see Ballschmiter et al. 1992). Twenty-nine PBDE congeners were measured including: IUPAC 28/33 (co-eluted), 47, 49, 66, 85, 99, 100, 116, 119, 138, 139, 140, 153, 154, 155, 179, 180, 183, 184, 196, 197, 201, 202, 203, 206, 207, 208, and 209. ΣPBDE values were the sum of these congeners.

Statistical analysis

Correlation analysis (StatSoft 2005) was used to examine relationships between time, egg $\delta^{15}N$ values, egg FA values, contaminant levels, and fish abundance data. Data regarding total warm-water fish abundance were collected by the New York State Department of Environmental Conservation (Klindt 2006). These data consisted of an annual (1986–2005) index of total fish (31 species) abundance from Lake St Lawrence. Because herring gulls may preferentially consume particular species based upon their vulnerability to gull predation this is only a coarse measure of fish availability to herring gulls. However, these are the best data summarizing temporal variation in fish abundance in this section of the St Lawrence River. In all tests, $P < 0.05$ was deemed to be significant.

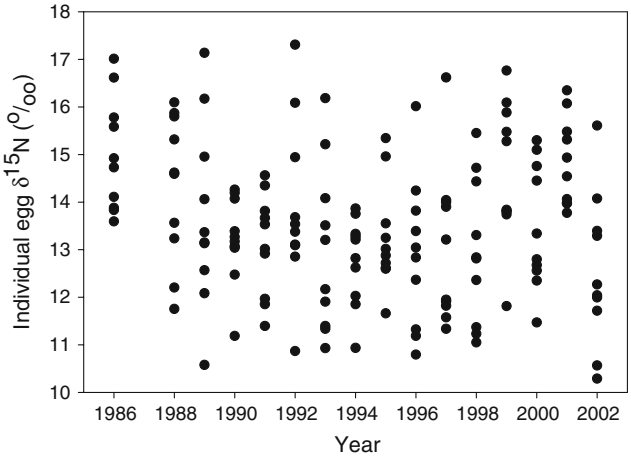

Fig. 1 Stable N isotope ratio ($\delta^{15}N$) values in individual herring gull (*Larus argentatus*) eggs collected from Strachan Island, St Lawrence River, Canada, 1986–2002. Data for individual eggs were not available for 2003–2005

Principal components analysis (PCA) using correlation matrices was used to further investigate patterns in the congener-specific, PCB, and PBDE concentration data for individual eggs collected during 2001–2002 (StatSoft 2005). For this analysis, PCB and PBDE homologs (i.e., groups of congeners having the same number of halogen atoms) were used. Homologs (for PCBs, Cl_3–Cl_9; for PBDEs, Br_3–Br_{10}) were calculated by summing the concentrations of individual congeners within each homolog group.

Results

There was considerable intra- and inter-year variation in egg $\delta^{15}N$ values (Fig. 1). However, there was no significant temporal trend in egg $\delta^{15}N$ values from 1986 to 2005 ($r = -0.16$, $P = 0.51$). Annual egg $\delta^{15}N$ values were positively correlated with egg n-3/n-6 FA ratios ($r = 0.65$, $P = 0.01$; Fig. 2) and with an index of fish abundance from the same area ($r = 0.46$, $P = 0.05$; Fig. 3).

For the individual eggs analyzed during the 2001–2002 period, egg $\delta^{15}N$ values were correlated with egg n-3/n-6 FA ratios ($r = 0.57$, $P = 0.01$). Concentrations of most major contaminants, i.e., Hg ($r = 0.66$, $P = 0.01$), β-HCH

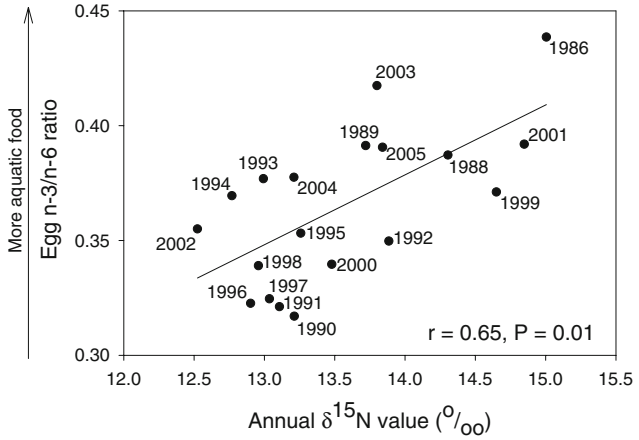

Fig. 2 Correlation between annual mean δ^{15}N values and n-3/n-6 fatty acid (FA) ratios in eggs collected from Strachan Island, St Lawrence River, 1986–2005. Year is denoted beside each point

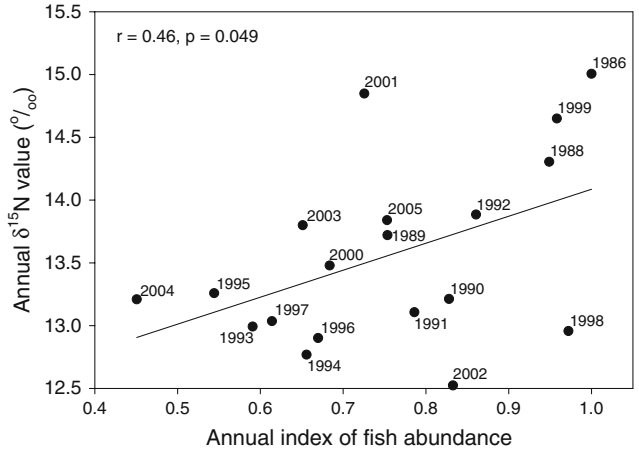

Fig. 3 Correlation between annual mean egg δ^{15}N values from Strachan Island and an annual index of fish abundance from Lake St Lawrence in the St Lawrence River, 1986–2005. Year is denoted beside each point. Fish data were collected by the New York Department of Environmental Conservation (Klindt 2006)

($r = 0.60$, $P = 0.01$), dieldrin ($r = 0.51$, $P = 0.02$), mirex ($r = 0.50$, $P = 0.02$), OCS ($r = 0.61$, $P = 0.01$), Σchlordanes ($r = 0.43$, $P = 0.06$), ΣDDT ($r = 0.52$, $P = 0.02$), ΣPCBs ($r = 0.56$, $P = 0.01$), and Σchlorobenzenes ($r = 0.43$, $P = 0.06$) were positively correlated with egg δ^{15}N values. Only ΣPBDE levels were not correlated with egg δ^{15}N values ($r = 0.17$, $P = 0.46$). Concentrations of individual contaminants varied greatly between the least and most contaminated eggs. Concentration (microgram per gram wet weight) ranges for contaminants measured above detection limits in all samples were as follows: dieldrin (0.002–0.081), mirex (0.117–0.754), OCS (0.001–0.021), Σchlordanes (0.012–0.238), ΣDDT (0.526–7.053), ΣPCBs (2.134–12.531), Σchlorobenzenes (0.002–0.038), and ΣPBDE (0.206–0.902). Hg concentrations ranged from 0.296 to 2.180 μg g^{-1} (dry wt). Different eggs collected during the 2001–2002 period exhibited up to a 41-fold difference in contaminant concentration.

Table 1 Variable loadings on principal component (*PC*) 1 and 2 from the PC analysis of polychlorinated biphenyl congeners (*PCB*) (Cl_3–Cl_9) and polybrominated diphenyl ethers (PBDE) (Br_3–Br_{10}) homolog concentration data

Homolog	Variable loadings	
	PC1	PC2
PCB Cl_3	**−0.84**	0.25
PCB Cl_4	**−0.80**	−0.13
PCB Cl_5	**−0.90**	−0.27
PCB Cl_6	**−0.90**	−0.19
PCB Cl_7	**−0.92**	−0.19
PCB Cl_8	**−0.91**	−0.16
PCB Cl_9	**−0.80**	−0.14
BDE Br_3	**−0.71**	−0.17
BDE Br_4	**−0.53**	0.08
BDE Br_5	**−0.59**	−0.02
BDE Br_6	**−0.60**	**0.55**
BDE Br_7	−0.19	**0.87**
BDE Br_8	−0.15	**0.93**
BDE Br_9	−0.12	**0.70**
BDE Br_{10}	−0.14	**0.65**

Results of the PCA of the 2001–2002 PCB and PBDE homolog data are shown in Table 1. Principal components 1 (PC1) and 2 (PC2) explained 67% of the variation in the data. Variable loadings on PC1 (46%) were dominated by all the PCB homologs (Cl_3–Cl_9) as well as the lower brominated PBDE homologs (Br_3–Br_6). Variable loadings on PC2 (21%) were dominated by the higher brominated PBDE homologs (Br_7–Br_{10}). Differences among individual eggs in their δ^{15}N values and PCB and PBDE composition are summarized in Fig. 4. Eggs with greater δ^{15}N values had higher PC1 scores. That is, levels of all PCB homologs and lower brominated PBDE homologs were greater in these eggs. Eggs with lower δ^{15}N generally were less contaminated with these PCB and PBDE homologs. However, eggs with lower δ^{15}N values generally had higher levels of the higher brominated PBDE homologs (Br_7–Br_{10}) as indicated by their PC2 scores.

Discussion

Temporal trends in N isotopes and FAs

There was considerable inter-year variation in egg δ^{15}N values (Fig. 1). It is probable that individual differences in laying-female foraging habits and resultant diet composition regulated annual differences in egg δ^{15}N and n-3/n-6 FA ratios. Temporal variation in diet composition was likely related to the availability of prey fish to foraging gulls. Because fish occupy higher trophic positions than

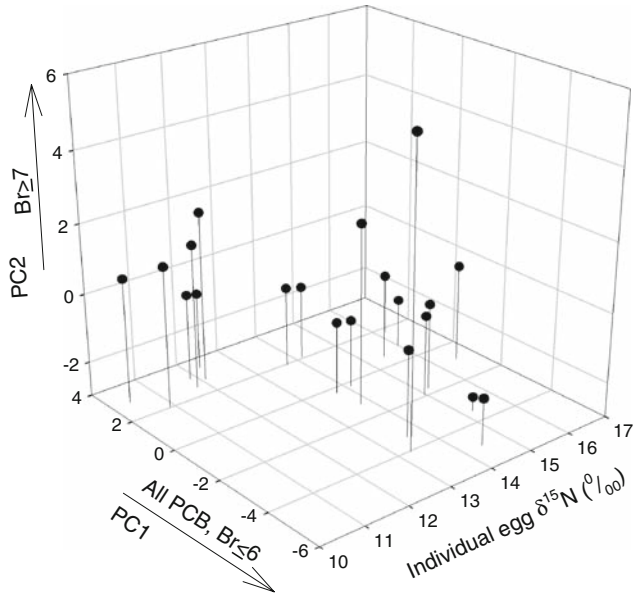

Fig. 4 Relationships among individual egg δ^{15}N values and principal component (*PC*) 1 and 2 scores from the PC analysis of polychlorinated biphenyl (*PCB*) and polybrominated diphenyl ether (PBDE) homolog concentration data. Individual eggs included here were collected in 2001 and 2002. Eggs with more negative PC1 scores have higher levels of all PCB homologs (Cl_3–Cl_9) and tri- up to and including hexa-PBDE homologs. Eggs with more positive PC2 scores have higher levels of higher brominated PBDEs (Br_7–Br_{10})

other prey that herring gulls consume (Hebert et al. 1999b), gulls consuming fish will lay eggs with greater δ^{15}N values. Here, we observed a positive relationship between annual mean egg δ^{15}N values and an index of warm-water fish abundance for the St Lawrence River. The "noise" in this relationship may have reflected inter-year differences in the degree to which individual fish species constituted fish abundance estimates versus which species were actually being consumed by gulls. Nevertheless, during years of greater fish abundance, gull egg δ^{15}N values also increased. The relationship observed here is similar to those observed between annual estimates of prey fish abundance and egg δ^{15}N values in each of the five Laurentian Great Lakes (Hebert et al. 2008). Diet composition was also reflected in egg FA profiles. In years of high fish abundance, when egg δ^{15}N values were greater, egg n-3/n-6 FA ratios also increased indicating that a greater proportion of the gull diet was originating from aquatic sources.

Correspondence among annual estimates of fish abundance, egg stable N isotope values, and egg FA profiles suggests that it is unlikely that shifts in δ^{15}N values at the base of the food web were responsible for the temporal variation observed in egg δ^{15}N values. If base-line shifts were responsible we would not have expected to see a correlation between δ^{15}N values and n-3/n-6 FA ratios. Furthermore, we would have expected to observe δ^{15}N values in gull eggs to gradually change through time. However, examination of long-term data regarding egg δ^{15}N values indicated no significant temporal trend (Fig. 1). Finally, if baseline change was responsible, similar egg δ^{15}N values would have been expected within a particular year. Examination of individual egg δ^{15}N values within and among years (1986–2002) indicated that within-year variation (maximum range = 6.6‰) was of the same magnitude as between-year variation (maximum range = 7.0‰). Therefore, we believe it is more reasonable to conclude that individual differences in foraging habits were responsible for the observed differences in egg δ^{15}N values.

Ecological tracer profiles in individuals

Analysis of individual eggs within years showed marked variation in δ^{15}N values (Fig. 1). Results from the analysis of individual eggs from 2001 to 2002 indicated that egg δ^{15}N values were correlated with egg n-3/n-6 FA ratios. Individuals laying eggs with greater δ^{15}N values incorporated a greater proportion of aquatic prey into their diets. Individual dietary preferences were further evident in the results of the contaminant analyses.

Organisms occupying higher trophic positions generally accumulate greater concentrations of bioaccumulating and biomagnifying contaminants such as methyl-Hg and organochlorines including PCBs and PBDEs. Therefore, traditional thinking would suggest that levels of such contaminants in eggs laid by females consuming more fish (which occupy higher trophic positions than other prey) would be greater (see Hebert et al. 2000). Results of the analysis of the 2001–2002 samples were consistent with these hypotheses. For all major organochlorines and Hg, positive correlations were observed between egg δ^{15}N values and contaminant concentrations. However, this relationship was not observed for ΣPBDE. The lack of a relationship between ΣPBDE and trophic position was possibly the result of differences among PBDE congeners in their primary pathways of transfer, namely aquatic versus terrestrial food webs.

PBDE patterns in aquatic organisms are dominated by the lower brominated PBDE congeners, i.e., IUPAC 47, 99, and 100. These congeners are usually found at the highest levels in most wildlife; however, in wildlife associated with terrestrial food webs, the highly brominated congeners, i.e., 183, 196, 197, 207, 209, predominate (Lindberg et al. 2004; Chen et al. 2007). Terrestrial prey may contain higher levels of highly brominated PBDEs than aquatic prey but the former will likely occupy lower trophic positions (see Hebert and Sprules 2002). We recently suggested that temporally changing aquatic versus terrestrial diet sources in herring gulls, and resulting PBDEs in eggs (collected from sites from each of the Great Lakes) could at least partly explain the increasing proportion of higher brominated

PBDE congeners (i.e., Br_8–Br_{10}), in more recently collected eggs; i.e., post-2000 (Gauthier et al. 2008). Therefore, trophic position may not be the most important factor regulating levels of PBDEs; instead, the critical factor may be the type of food exploited. Here, there is evidence that pathways of exposure for the lower brominated PBDEs ($\leq$6 Br atoms) are similar to those of the legacy organochlorines and Hg. However, the highly brominated PBDEs ($\geq$7 Br) behave differently. Differential use, and ultimately disposal, of products containing different commercial PBDE formulations may have ultimately been responsible for differences in PBDE congener/homolog routes of transfer.

Temporal changes and individual differences in egg ecological tracer profiles were useful in characterizing the gull diet but they are also important for what they may mean to the health of individual birds. Variability in diet composition caused organochlorine levels to vary up to 41-fold among the individual eggs collected in 2001–2002. From a risk assessment perspective, it is evident that variability in diet composition regulates exposure to persistent contaminants and needs to be considered when assessing the potential for contaminant effects in individual birds.

Temporal alterations in the isotopic and FA composition of eggs reflected changes in the availability of aquatic prey, namely fish. Similar results have been reported in the Laurentian Great Lakes (Hebert et al. 2008). In that region, food webs have changed greatly through time. Exotic species introductions, fishing, habitat loss, and nutrient inputs have all been implicated in these changes (United States Environmental Protection Agency 2001). For gulls, declines in fish abundance and availability have lessened the predominance of fish in their diet with terrestrial foods becoming more important. These changes have affected egg FA composition most notably through temporal declines in the proportion of n-3 FA in eggs. Omega-3 FA, e.g., eicosapentaenoic acid (20:5n-3), docosapentanoeic acid (22:5n-3), and docosahexaenoic acid (22:6n-3) are termed essential because they are necessary for normal growth and development and because they typically cannot be produced (through elongation and desaturation of the shorter chain omega-3 alpha-linoleic acid) in quantities sufficient to sustain optimal physiological performance. Decreased availability of n-3 FA and other essential FA to gulls as a result of dietary shifts could be adversely affecting the health of individuals, the viability of their eggs and offspring, and the sustainability of gull populations.

Gulls preferentially prey on fish when they are abundant but, as fish availability declines, some birds may shift from fish to other prey types, particularly easy-to-obtain garbage. Diet composition regulates the nutritional status of individuals which, in turn, can affect individual fitness (Metcalfe and Monaghan 2001). Fish are a high-quality food rich in energy and nutrients (Wanless et al. 2005). The ramifications to breeding herring gulls of consuming prey of lower nutritional quality are known from Lake Superior (Hebert et al. 2002). Gulls are in poorer condition and demonstrate reduced reproductive success in areas where they rely more on terrestrial prey (Hebert et al. 2002). Shifts in the proportions of individuals utilizing certain types of food may be indicative of changes in food web dynamics as a result of changes in the relative abundance of prey. Changes in the distribution of individuals consuming certain prey types may provide the means to identify ecosystem change and act as early warning indicators of such change.

The use of multiple ecological tracers to address changes in ecosystem processes and food web structure is still in its infancy. Different tracers provide unique but complementary insights into food web relationships. There are costs and benefits associated with each group of tracers. Stable N isotopes can provide insights into change in trophic position but are limited in their ability to provide detailed insights into dietary change. FA may be able to provide such detailed information but sample storage requirements are stringent and detailed information on prey FA signatures is required for comparison. Biomagnifying contaminants are useful food web tracers because of the limited degree to which they are transformed during trophic interactions; however, analytical costs are high. One advantageous trait that all these groups of tracers have in common is their amenability to retrospective analysis. This is important because retrospective analysis of archived samples can provide an historical perspective on how food web relationships have changed through time, putting recent change into context and provide a historical perspective to guide future management decisions (Hebert et al. 2008).

In this study, the application of stable N isotopes, FAs, and bioaccumulating contaminants to examine dietary variation in a single species was successful. This was in large part a reflection of the catholic diets of herring gulls. Omnivory is a common trait in high trophic level predators (Thompson et al 2007); therefore, the approach described here could be broadly applicable to assessing pathways of energy, nutrient, and contaminant flow in other species. In the future, the integrated application of multiple ecological tracers will undoubtedly lead to new insights in the field of food web ecology.

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