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# Changes in Food Web Structure Affect Rate of PCB Decline in Herring Gull (*Larus argentatus*) Eggs

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Biological monitors provide important information regarding temporal trends in levels of persistent organic pollutants. Correct interpretation of these trends is critical if we are to accurately assess our progress in eliminating these contaminants from the environment. In the Laurentian Great Lakes, polychlorinated biphenyl concentrations in herring gull eggs declined during the 1970s and early 1980s. By the mid-1980s, further declines were not as obvious. An exception to this trend was observed in eggs from Lake Erie. On that lake, egg PCB concentrations continued to decline rapidly during the 1980s/1990s. Evidence from stable isotope analysis indicated that temporal changes in the composition of the herring gull diet occurred on Lake Erie. In the eastern basin, declines in fish availability may have forced the gulls to incorporate a greater proportion of terrestrial food into their diets. Decreases in the proportion of fish in the gull diet would have resulted in reduced PCB exposure. This may be partially responsible for the continuing rapid rate of decline in egg PCB concentrations. This decline should be interpreted with caution. These trends may not be indicative of lake-wide declines in PCB bioavailability but only reflect changes in dietary exposure brought about by alterations in food web structure.

## Introduction

The Great Lakes Herring Gull Monitoring Program (GLHGMP) has evaluated temporal trends in organochlorine contaminants in the Laurentian Great Lakes since the early 1970s (*1, 2*). Because of their toxicological importance, particular interest has been paid to evaluating temporal declines in levels of polychlorinated biphenyls (PCBs). Following restrictions on PCB use imposed in the 1970s, egg PCB concentrations declined rapidly until the early 1980s. However, since the mid-1980s trends have not been as obvious. It appears that while egg PCB levels are still declining, the rate of decline has slowed (*3, 4*). This seems to be the general situation in all of the Great Lakes with the exception of Lake Erie. On that lake, there is some evidence that egg levels have continued to decline rapidly (*3, 5*).

Examination of temporal trends in Lake Erie walleye (*Stizostedion vitreum*) (1977−1995) shows that whole fish PCB concentrations declined in the late 1970s but, despite annual fluctuations, have remained relatively stable since then (*6*). PCB concentrations in Lake Erie rainbow smelt (*Osmerus mordax*) (1977−1994) and lake trout (*Salvelinus namaycush*) (1984−1995) show little evidence of a temporal decline (*6*).

Rapid declines in herring gull egg PCB levels may be indicative of the continued rapid removal of PCBs from the Lake Erie ecosystem following restrictions on their use. However, this is not consistent with the trends observed in fish. Furthermore, the fact that PCB declines in gull eggs from the other lakes and connecting channels have slowed (*3*) would suggest that this scenario is unlikely unless remedial measures to eliminate PCBs from Lake Erie have been more effective than in the other lakes. A major source of PCBs and other organochlorines to Lake Erie is the Detroit River (*7, 8*). Trends in eggs of herring gulls nesting on Fighting Island in the Detroit River should be indicative of temporal changes in PCB loadings/bioavailability in that system. We would expect that changes in PCB bioavailability in the Detroit River would be important in regulating PCB exposure to gulls nesting on Lake Erie. Therefore, if PCB loadings are most important in regulating PCB exposure in Lake Erie herring gulls, we would expect that trends in gulls nesting on the Detroit River and in Lake Erie should be similar. If they are not, then other factors may be more important in regulating PCB exposure in Lake Erie gulls.

Another possible explanation for the continued rapid decline in Lake Erie egg PCB concentrations is dietary change. Because the dominant route of PCB bioaccumulation is through food, it is possible that changes in the herring gull diet may have also contributed to the observed trends. In Lake Ontario, annual fluctuations in egg PCB concentrations are influenced by changes in the composition of the herring gull diet (*9*). On the Great Lakes, herring gulls are primarily piscivorous but they also consume a wide variety of other food types including garbage, small mammals, invertebrates, songbirds, amphibians, and vegetation (*10−12*). Different dietary items would be expected to vary in their degree of PCB contamination. Hence, changes in herring gull diet composition would alter their exposure to PCBs.

An integral component of this study was to assess temporal changes and individual differences in the composition of the herring gull diet. As part of the GLHGMP, egg samples are archived in the specimen bank at the National Wildlife Research Centre, Hull, Québec. This has allowed us to quantify changes in the herring gull diet by analyzing gull eggs from Lake Erie using naturally occurring stable nitrogen ($^{15}N/^{14}N$) and carbon ($^{13}C/^{12}C$) isotopes.

Stable isotopes have been used to examine energy flow through food webs (*13*). Stable nitrogen isotopes have been used to elucidate food web interactions and to estimate species trophic position (*12, 14−16*). This is possible because during trophic interactions the heavy $^{15}N$ isotope is enriched relative to the lighter $^{14}N$ isotope resulting in an increase in $\delta^{15}N$ values by 3−4‰ from one trophic level to the next (*13, 14*). This also applies to avian eggs; Hobson (*17*) found that $\delta^{15}N$ values in egg protein were 3.4‰ greater than those in the laying female's diet.

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**FIGURE 1. Locations of herring gull monitoring colonies sampled annually as part of the Great Lakes Herring Gull Monitoring Program. 1, Granite Island; 2, Agawa Rocks; 3, Gull Island; 4, Big Sister Island; 5, Double Island; 6, Chantry Island; 7, Saginaw Bay; 8, Fighting Island; 9, Middle Island; 10, Port Colborne; 11, Niagara River; 12, Toronto Harbor; 13, Snake Island.**

Unlike $\delta^{15}N$, $\delta^{13}C$ shows little consistent trophic enrichment (*13*). However, $^{13}C$ and $^{12}C$ react at different rates in biogeochemical reactions resulting in differences in $\delta^{13}C$ signatures among major carbon sources. These differences have been used to determine the origin of carbon inputs into food webs (*18, 19*). For example, primary producers in terrestrial and lake ecosystems have different $\delta^{13}C$ signatures (*18*). In general, phytoplankton exhibit more negative $\delta^{13}C$ signatures (−32‰ to −46‰) than those measured in terrestrial C-3 foliage (−28‰) (*18*−*20*). In large lakes, most autochthonous primary production is in the form of phytoplankton (*21*). By using $\delta^{15}N$ and $\delta^{13}C$ measurements of eggs and food web components, we can gain insights into the composition of the herring gull diet.

In this paper, we investigate temporal trends in egg PCB concentrations from each of the Great Lakes to determine whether rates of decline have changed through time. We then focus on explaining the trends observed in Lake Erie. This involved examining the relationship between diet composition, as measured using stable nitrogen and carbon isotopes, and egg PCB concentrations.

## Materials and Methods

**Egg Collections.** Herring gull eggs were collected annually by the Canadian Wildlife Service (CWS) from the 13 colonies incorporated into the GLHGMP. These colonies are located on all five of the Great Lakes (Figure 1). As part of a study examining diet quality in Great Lakes herring gulls, egg samples were also collected from another colony (Mohawk Island) in the eastern basin of Lake Erie in 1996. This colony is approximately 20 km west of the GLHGMP colony at Port Colborne. All of the samples were stored at −40 °C until analyzed. Further details regarding sample collection, storage, and processing have been reported previously (*1*).

**PCB Analysis of Great Lakes Herring Gull Eggs.** PCB analyses were undertaken to address two questions: (a) temporal data from all 13 Great Lake colonies were examined to determine whether the rate of decline of total PCB levels changed through time and (b) data from individual eggs collected in 1996 from Mohawk Island were examined to investigate the relationships between PCB levels and diet (as inferred from stable isotopes).

To address the first question, homogenates of 10−13 whole eggs per colony were pooled on an equal weight basis for each year. Organochlorine analyses were completed according to the methodology described in Norstrom et al. (*22*). Routinely within the GLHGMP, 71 PCB congeners are measured in addition to 22 other organochlorines. In this paper, we focus on the PCBs because of their toxicological significance. Most of the data (1979−1997) analyzed in this paper have been reported elsewhere (*23*−*25*). Total PCB concentrations reported in this section are 1:1 Aroclor 1254:1260 estimates. In herring gull eggs, Aroclor estimates of total PCB concentrations overestimate total PCB concentrations calculated using the sum of individual congeners by 1.7−2.2 times. The former value is based upon comparisons using sum of PCB values based upon 71 congeners (this study). The latter value is based upon older comparisons using 41 congeners completed by Turle et al. (*26*).

To address the second question, 10 individual herring gull eggs collected in 1996 from Mohawk Island were analyzed. Organochlorine analyses were conducted in an identical manner as described above. The data were used to examine the relationships between concentrations of total PCBs (both sum of 71 congeners and Aroclor 1:1 values), PCB homologues, and individual PCB congeners with egg stable isotope values.

**Stable Isotope Analysis of Lake Erie Herring Gull Eggs.** Using a similar rationale described for the organochlorine analyses, stable isotope analyses were performed to address two questions: (a) stable isotope data from Lake Erie were examined to determine whether there had been temporal changes in the stable isotope signatures of herring gull eggs and (b) individual eggs were analyzed to investigate the relationships between diet (as inferred from stable isotopes) and PCB levels. We assumed that changes in stable isotope composition through time would reflect real dietary or trophic changes rather than baseline isotopic changes in the food web (see ref *12*). For a summary of the entire Great Lakes egg isotope data set prior to 1996, see ref *12*.

To address (a), egg samples collected from 1982 to 1997 from the two Lake Erie GLHGMP colonies (Middle Island and Port Colborne) were analyzed. For samples collected from 1982 to 1989, individual homogenates of the 13 eggs from each colony were pooled by colony and year on an equal weight basis; therefore, only one combined sample was analyzed from each of the two colonies each year. These pools were identical to those used for organochlorine analysis. Eggs collected from 1990 to 1997 were analyzed individually. When isotopic results from individual samples were available, a mean stable isotope value was calculated, and this mean value was used in the examination of temporal trends. Data are not available from Port Colborne for 1984 or 1994.

To address (b), stable isotope analysis was conducted on 10 individual eggs collected in 1996 from Mohawk Island. Results of these analyses were used to investigate the relationships between diet (as inferred from stable isotopes) and PCB levels.

All stable isotope analyses were completed using the methods summarized below. One milliliter subsamples of the pooled herring gull egg homogenates or individual eggs were freeze-dried, and lipids were removed using several 2:1 chloroform:methanol rinses. Stable nitrogen and stable carbon isotope analyses were conducted on these lipid-free subsamples. For $\delta^{15}N$ and $\delta^{13}C$ analysis, approximately 1 mg of powdered sample was weighed into tin cups and combusted at 1800 °C in a Robo Prep elemental analyzer 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. Stable nitrogen and carbon isotope ratios were expressed in delta ($\delta$) notation, as parts per thousand (‰) deviation from a standard. Nitrogen and carbon stable isotope standards were atmospheric nitrogen and Pee Dee Belemnite limestone, respectively. On the basis of hundreds of replicate measurements of lab standards, we estimate analytical precision to be ±0.1‰ for carbon and ±0.3‰ for nitrogen.

**Statistical Analysis.** Linear regression was used to examine temporal trends in log egg PCB concentrations during two

**TABLE 1. Comparison of the Rate of Decline in Egg PCB Concentrations between Two Periods, 1979−1988 and 1989−1998[a]**

| colony | slope 1979−1988 | slope 1989−1998 | change in rate | % change |
|---|---|---|---|---|
| 1, Granite | 0.0617 | 0* | slower | 100 |
| 2, Agawa | 0.0729 | 0.0288 | slower | 60 |
| 3, Gull | 0.0767 | 0* | slower | 100 |
| 4, Big Sister | 0.0531 | 0* | slower | 100 |
| 5, Double | 0.0495 | 0.0331 | slower | 33 |
| 6, Chantry | 0.0704 | 0.0319 | slower | 55 |
| 7, Saginaw | 0.0400 | 0.0295 | slower | 26 |
| 8, Fighting | 0.0555 | 0.0432 | slower | 22 |
| 9, Middle | 0.0305 | 0.0376 | faster | 23 |
| 10, Colborne | 0.0474 | 0.0562 | faster | 19 |
| 11, Niagara | 0.0744 | 0.0389 | slower | 48 |
| 12, Toronto | 0.0738 | 0.0401 | slower | 46 |
| 13, Snake | 0.0593 | 0.0255 | slower | 57 |

[a] Slopes of the time−concentration regression lines indicate the rate at which egg PCB concentrations declined through time. Larger slopes indicate more rapid rates of decline. An asterisk (*) indicates to see text for details.

periods: 1979−1988 and 1989−1998. These periods were chosen somewhat arbitrarily but represent convenient 10-year periods for comparative purposes. The slopes of the time−concentration regression lines provided an indication of the rapidity of PCB decline. Percent change in the rate of decline between the two periods was calculated as ($slope_{79-88}$ − $slope_{89-98}$)/$slope_{79-88}$ × 100. At three colonies (1, 3, 4), the slope of the time−concentration regression from 1989 to 1998 was not statistically different from zero. At these locations, the change in the rate of PCB decline was deemed to be 100%.

Linear regressions were used to examine temporal trends in egg stable nitrogen and carbon isotopes. Nonlinear models were used to determine whether there were relationships between prey fish abundance and egg stable isotope values (see Figure 5 for model equations).

The relationship between egg PCB concentrations and stable isotope values was investigated using the individual Mohawk Island samples collected in 1996. Utilization of individual eggs from one year avoided confounding temporal effects on PCB concentrations. Spearman rank correlations were used to evaluate the significance of these relationships.

## Results and Discussion

At all Great Lakes colonies, with the exception of those on Lake Erie, rates of PCB decline were slower during the 1989−1998 period than during the 1979−1988 period (Table 1). The average reduction in the rate of PCB decline in eggs collected from outside Lake Erie was approximately 60%. At both Lake Erie colonies, the rate of decline increased approximately 20%. That is, Lake Erie egg PCB concentrations declined 20% faster during 1989−1998 than during 1979−1988. It is interesting to note that the rate of PCB decline slowed in eggs from the Detroit River colony (Fighting Island). If remedial measures associated with cleaning up the Detroit River were of paramount importance in affecting PCB concentrations in eggs from Lake Erie, then we would have expected a decrease in the rate of PCB decline in Lake Erie eggs as well. This result suggests that the increased rate of PCB decline observed at both Lake Erie colonies is the result of another mechanism.

A detailed examination of the geographic and temporal trends in egg stable isotope values from all of the Great Lakes has been published previously (*12*). A pertinent finding of that paper was that the most significant temporal changes in egg isotope values were observed in Lake Erie. Evidence

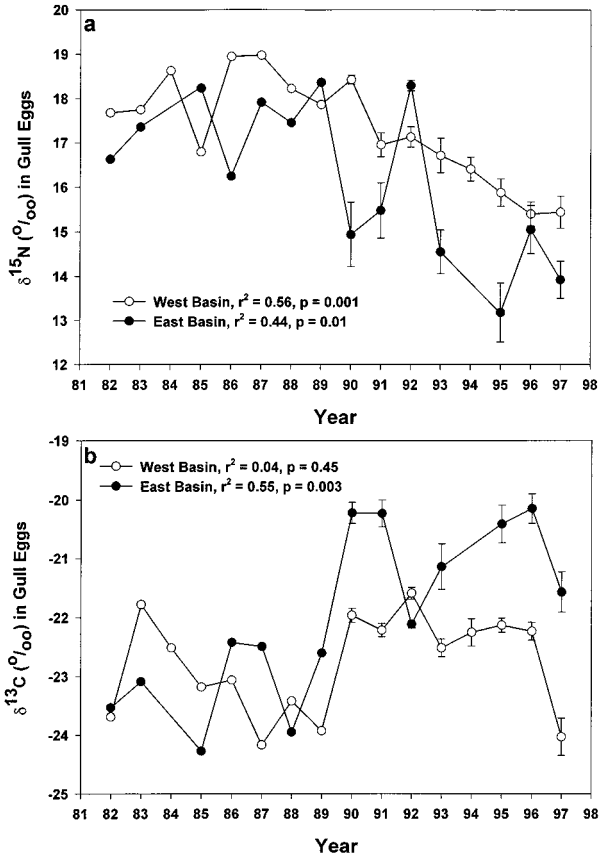


**FIGURE 2. Temporal trends in egg stable isotope values, (a) $\delta^{15}N$ and (b) $\delta^{13}C$, from the two annual monitoring colonies located on Lake Erie. West basin is Middle Island; east basin is Port Colborne. Error bars represent 1 SE.**

from the $\delta^{15}N$ and $\delta^{13}C$ analyses suggested that there were major changes in the composition of the Lake Erie herring gull diet through time. At both Lake Erie colonies, significant temporal declines in $\delta^{15}N$ values were observed (Figure 2a). In the eastern basin of the lake, $\delta^{13}C$ increased significantly through time (Figure 2b) while in the western basin no significant temporal trends in $\delta^{13}C$ were observed (Figure 2b). Hebert et al. (*12*) discuss some of the possible reasons for these changes. In this paper, we focus on explaining trends in eastern Lake Erie because the largest changes in $\delta^{15}N$ and $\delta^{13}C$ were observed in that region and the rate of decline in egg PCB concentrations during the 1989−1998 period was more rapid there than at any other Great Lakes colony (Table 1).

In eastern Lake Erie, the rainbow smelt is the most abundant prey fish species. However, smelt abundance in the eastern basin has declined through time (Figure 3). These changes in smelt abundance would be expected to affect fish availability to the herring gull. Support for this hypothesis is provided by the significant relationships observed between estimates of rainbow smelt abundance and egg $\delta^{15}N$ and $\delta^{13}C$ values (Figure 4a,b). As smelt abundance increased, egg $\delta^{15}N$ increased and egg $\delta^{13}C$ decreased. The isotopic signatures of fish are enriched in $^{15}N$ and somewhat depleted in $^{13}C$ as compared to other dietary items (*12*). Examination of stable isotope signatures of fish and terrestrial food items suggested that a switch from smelt to other prey fish species could not account for the changes in egg isotope values (see ref *12*), instead, these changes were probably the result of a shift in the herring gull diet from fish to terrestrial prey.

Data previously collected by CWS (R. Norstrom, unpublished) indicates that with an increasing proportion of fish in the herring gull diet exposure to PCBs increased (Figure

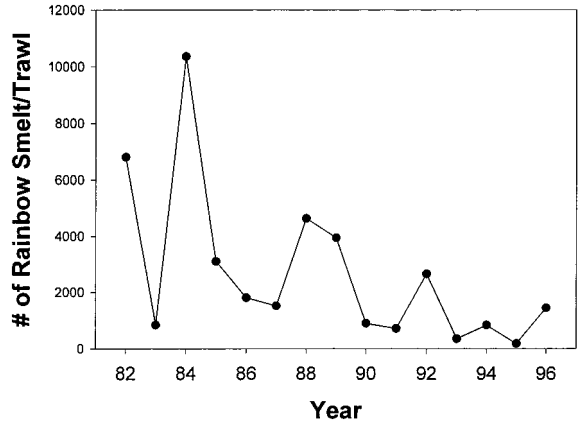


**FIGURE 3. Temporal declines in estimates of rainbow smelt abundance in the eastern basin of Lake Erie. Data are from the Pennsylvania Fish and Boat Commission (*34*).**

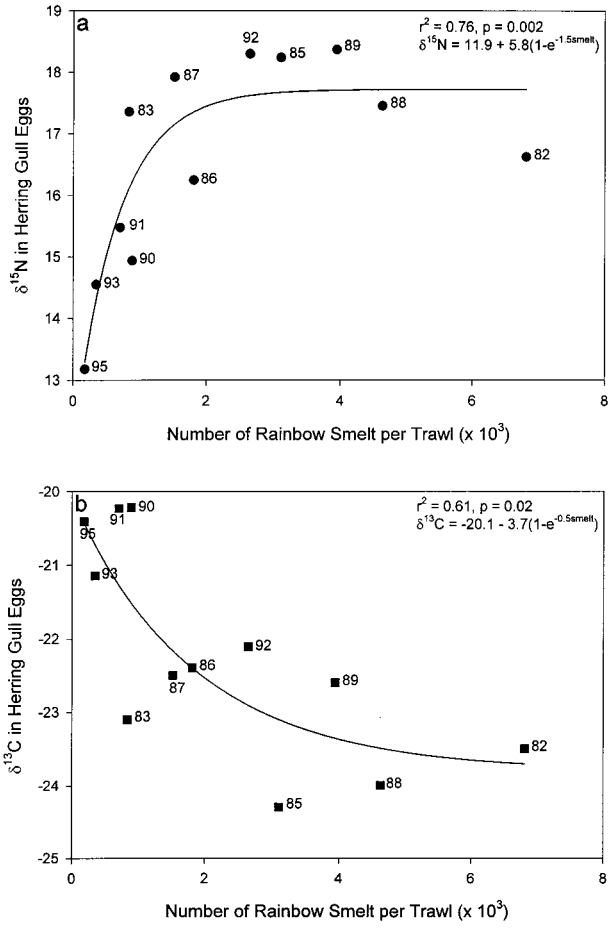


**FIGURE 4. Relationship between estimates of smelt abundance and egg stable isotope values: (a) $\delta^{15}$N and (b) $\delta^{13}$C. Eggs were collected from Port Colborne. Smelt data are from the Pennsylvania Fish and Boat Commission (*34*).**

5). Therefore, with a decreased proportion of fish in the herring gull diet, PCB exposure would be expected to decrease, potentially resulting in the more rapid decline in egg PCB concentrations during the more recent period.

Support for this hypothesis is provided by results from the analysis of individual eggs collected from Mohawk Island in 1996. Preliminary examination of the relationship between egg total PCB concentrations and egg stable isotope values suggested that there were no relationships (Table 2). However, upon closer examination, it was evident that there were

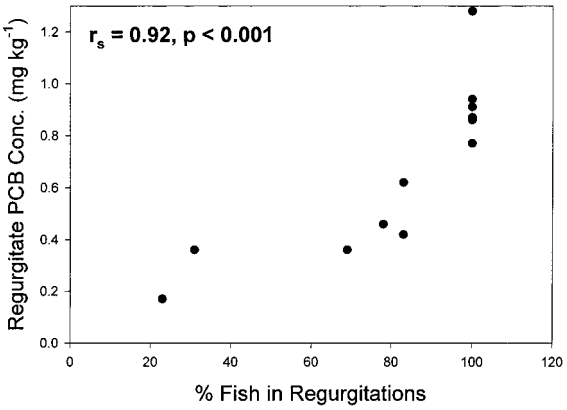


**FIGURE 5. Relationship between percent fish in herring gull regurgitations and regurgitate PCB concentration. Unpublished data were provided by R. Norstrom and represent samples collected from Lake Huron in May−June 1978.**

**TABLE 2. Spearman Rank Correlations between Egg PCB Concentrations and Egg Stable Isotope Values[a]**

| | egg $\delta^{15}$ N (‰) | | egg $\delta^{13}$ C (‰) | |
|---|---|---|---|---|
| egg PCB concn | Spearman *r* | p | Spearman *r* | p |
| $Cl_3$ homologue | 0.64 | 0.05 | −0.67 | 0.03 |
| $Cl_4$ homologue | 0.56 | 0.09 | −0.59 | 0.07 |
| $Cl_5$ homologue | 0.53 | 0.12 | −0.56 | 0.09 |
| $Cl_6$ homologue | 0.20 | 0.58 | −0.20 | 0.58 |
| $Cl_7$ homologue | 0.16 | 0.65 | −0.14 | 0.70 |
| $Cl_8$ homologue | 0.18 | 0.63 | −0.16 | 0.65 |
| $Cl_9$ homologue | −0.01 | 0.99 | 0.09 | 0.80 |
| Aroclor 1:1 | 0.26 | 0.47 | −0.27 | 0.45 |
| sum of congeners | 0.20 | 0.58 | −0.20 | 0.58 |

[a] Measurements were made using eggs from Mohawk Island, eastern Lake Erie, 1996 ($n$ = 10).

significant relationships between some of the PCB homologue groups and the stable isotope values (Table 2). The significance of these relationships diminished with an increase in the degree of chlorine substitution of the PCB molecule (Table 2). There were significant or marginally significant relationships between tri-, tetra-, and pentachlorinated homologues and egg stable isotope values. For all of the homologues, except for $Cl_9$, concentrations were positively associated with $\delta^{15}$N values and negatively related to egg $\delta^{13}$C. However, at increasing levels of chlorination (>$Cl_5$) no statistically significant (defined as $p < 0.1$) relationships were observed (Table 2).

Assuming that stored (endogenous) nutrients play little role in egg formation in these birds, stable isotope values in eggs will reflect the diet of the adult bird during the period of egg formation (*17*). In contrast, organochlorines deposited into the avian egg may be mobilized from adult lipid stores and may not reflect short-term contaminant exposure through the diet (*27*). This may occur if recently absorbed dietary lipids undergo hepatic reprocessing to produce egg yolk constituents with contaminant signatures similar to the adult female. This results in difficulties when trying to relate egg stable isotope values and contaminant levels, particularly for compounds with long half-lives. For those compounds, egg contaminant levels will reflect the adult's exposure over a long period while the egg isotope values will integrate diet composition over a shorter time frame. If exposure to these compounds varies through time, as a result of factors such as diet variation or migration, then egg contaminant concentrations and isotope values will not be correlated. For example, neither $\delta^{15}$N nor $\delta^{13}$C were correlated with total PCB concentrations (Table 2). Total PCB values are dominated

by a relatively few highly chlorinated congeners with very long half-lives (*28*) and high biomagnification potentials (*29*). Therefore, it was not surprising that there was no correlation between egg total PCB levels and stable isotope values. Results of the congener-specific analysis allowed us to examine the relationship between concentrations of individual congeners and egg stable isotope values leading to a better understanding of the utility of stable isotopes as indicators of egg contaminant concentrations.

Previous studies have demonstrated that there are large differences in the degree to which individual congeners are biomagnified and that the degree of biomagnification is primarily determined by their chlorine substitution pattern (*29, 30*). Congeners with adjacent unchlorinated meta-para positions on at least one of the phenyl rings [group IV and V congeners according to Boon et al. (*30*)] will be metabolized and eliminated much more rapidly than congeners that lack this structure (groups I, II, and III). A mean half-life for these readily metabolized congeners is approximately 50 days whereas the more persistent congeners have half-lives of approximately 500 days (*28*). Therefore, we would expect that the concentrations of the readily metabolized congeners would reflect more recent PCB exposure (i.e., coinciding with the period of egg formation). Because dietary routes of exposure are most important for PCBs, we would also expect that diet composition, as indicated by stable isotope values, would play an important role in determining concentrations of these congeners. When we examined relationships between congener concentrations and isotope values we found that the majority (~70%) of meta-para unchlorinated congeners [groups IV and V according to Boon et al. (*30*)] exhibited a significant relationship with egg isotope values (Figure 6a,b). In contrast, concentrations of congeners with different chlorine substitution patterns were rarely correlated with stable isotope values (Figure 6a,b). Congeners lacking adjacent unchlorinated meta-para positions but having unsubstituted ortho-meta positions [termed ortho-meta or groups II and III by Boon et al. (*30*)] showed some significant relationships with egg isotope values (10−30%). Those congeners lacking adjacent unsubstituted positions [termed blocked or group I by Boon et al. (*30*)] exhibited no significant correlations with egg isotope values.

It is evident from this analysis that the relationship between egg contaminant concentrations and stable isotope values is not straightforward. However, the relationships that were observed between metabolized PCB congeners (meta-para) and stable isotopes, both of which reflect environmental/dietary conditions during egg laying, provided evidence that as the proportion of fish in the herring gull diet declined, exposure to PCBs was reduced.

The temporal changes in the herring gull diet documented here likely resulted from a decline in prey fish availability brought about by recent changes in the Lake Erie ecosystem (*12, 31−33*). Increased rates of PCB decline in Lake Erie herring gull eggs in more recent years may not reflect changes in environmental loadings but instead reflect changes in exposure mediated through shifts in diet composition. If a rapid change in PCB bioavailability had occurred, we would have expected to observe a similar temporal decline in PCB concentrations in other monitoring species. However, PCB temporal trends in Lake Erie fish did not exhibit the overt, continuing decline observed in herring gull eggs.

These results emphasize the importance of food web interactions in regulating organochlorine exposure to wildlife. Correct interpretation of contaminant monitoring data requires that we consider the dynamic nature of ecosystems and the potential for changes in food web structure.

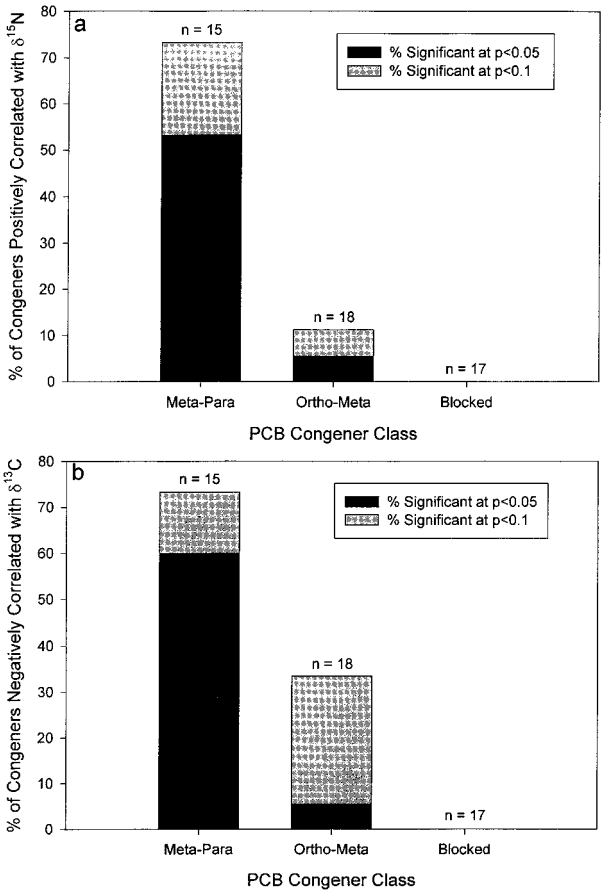


**FIGURE 6. Effect of congener chlorine substitution patterns on the relationship between congener concentrations and stable isotope values, (a) $\delta^{15}$N and (b) $\delta^{13}$C, in herring gull eggs. Meta-para and ortho-meta refer to congeners that have adjacent unchlorinated meta-para positions or ortho-meta positions, respectively. Blocked refers to congeners that lack any adjacent unchlorinated positions. Only the meta-para congeners showed a high proportion of significant relationships with egg isotope values (see text for details).**

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