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

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Introduction

The Herring Gull Monitoring Program has evaluated temporal trends in organochlorine contaminants in the Laurentian Great Lakes since the early 1970s. 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 (1). This seems to be the general situation in all of the Great Lakes with the exception of Lake Erie. On Lake Erie, egg levels have continued to decline rapidly (1,2).

In 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 (3-5). In Lake Ontario, annual changes in the composition of the herring gull diet have been shown to contribute to fluctuations in annual egg PCB concentrations (6). This paper will examine the possible role of dietary changes in explaining the continuing decline in PCB contamination of Lake Erie herring gull eggs.

Materials and Methods

Herring gull eggs were collected annually by the CWS from 13 colonies located on all five of the Great Lakes. Homogenates of 10 to 13 whole eggs per colony were pooled on an equal weight basis for each year. All of the samples were stored at -40 °C until analyzed. Congener-specific PCB analyses were completed following the methodology described in Norstrom et al. (7). Stable nitrogen and carbon isotope analyses were also conducted on these egg pools following the methods described in Hebert et al. (5). In addition, eggs collected from western and eastern Lake Erie in 1996 were analyzed individually for both organochlorines and stable isotopes.

Linear regression was used to examine temporal trends in egg PCB levels during two periods: 1979-88 and 1989-98. The slopes of the regression lines provided an indication of the rapidity of PCB decline through time.

Linear regressions were used to examine temporal trends in egg stable nitrogen and carbon isotopes. Non-linear models were used to determine whether there were relationships between prey fish abundance and egg stable isotope values. Stable isotope measurements were also made in potential herring gull prey. These prey items included fish collected from Lake Erie as well as terrestrial birds and garbage.

The relationship between egg PCB concentrations and stable isotope values was investigated using the individual Lake Erie 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 1989-98 period than during the 1979-88 period (Figure 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% (i.e. egg PCB concentrations declined 20% faster during 1989-98 than during 1979-88).

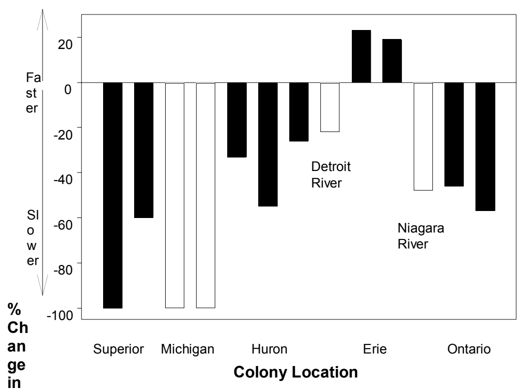

Figure 1. Change in the rate at which herring gull egg PCB concentrations declined through time. Rate of decline was compared between two periods, 1979-88 and 1989-98. Each bar represents trends at one Great Lakes colony. At all colonies, except in Lake Erie, the rate of decline slowed.

Stable nitrogen and carbon isotope values in Great Lakes herring gull eggs changed through time. The most pronounced changes were observed in eggs from Lake Erie (see 5). At both Lake Erie colonies, $\delta^{15}N$ values declined significantly through time (west basin, slope=-0.19, r^2=0.56, p=0.001; east basin, slope=-0.24, r^2=0.44, p=0.01). In the eastern basin of the lake, $\delta^{13}C$ increased significantly through time (slope=0.22, r^2=0.55, p=0.003) while in the western basin no significant temporal trends in $\delta^{13}C$ were observed (r^2=0.04, p=0.45). Because the largest changes in $\delta^{15}N$ and $\delta^{13}C$ were observed in eastern Lake Erie we focus on explaining trends in eggs from that region.

In eastern Lake Erie, significant relationships were observed between estimates of prey fish (rainbow smelt, *Osmerus mordax*) abundance and egg $\delta^{15}N$ and $\delta^{13}C$ values (Figure 2). As smelt abundance increased, egg $\delta^{15}N$ increased and egg $\delta^{13}C$ decreased. Examination of stable isotope signatures of fish and terrestrial food items (see 5) suggested that the shifts in herring gull egg stable isotope values were probably the result of a shift in the herring gull diet from fish to terrestrial prey.

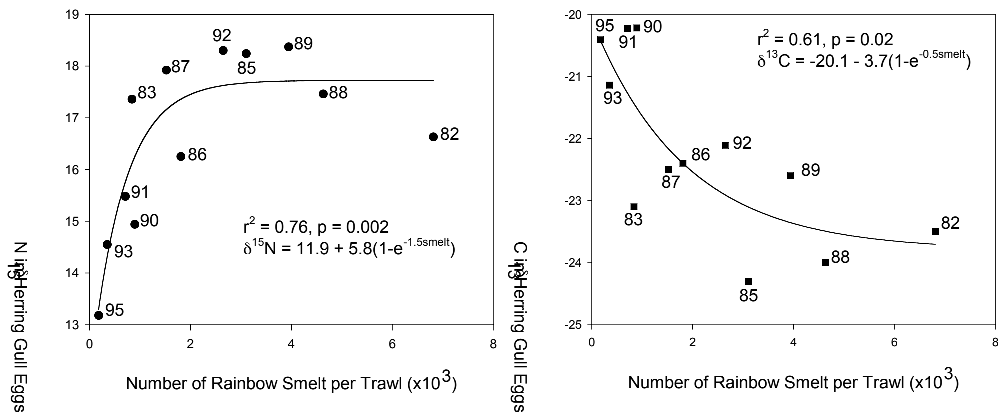

Figure 2. The relationship between annual estimates of prey fish abundance and stable isotope values in herring gull eggs. Data are from eastern Lake Erie. The numbers beside each point indicate year of collection.

Data previously collected by CWS indicates that with an increasing proportion of fish in the herring gull diet exposure to PCBs increased (CWS, unpublished). 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 was observed in the analysis of individual eggs collected in 1996. Stable isotope values in eggs reflect the diet of the adult bird during the period of egg formation (8). In contrast, organochlorines deposited into the avian egg may be mobilized from adult lipid stores and may not reflect a similar time frame to the period integrated by egg stable isotope measurements. This temporal discontinuity was reflected in the lack of correlation between either $\delta^{15}N$ or $\delta^{13}C$ and total PCB concentrations. Total PCB values are dominated by a relatively few highly chlorinated congeners with very long half-lives (9) and high biomagnification potentials (10). Therefore, it was not surprising that there was no correlation between egg total PCB levels and stable isotope values. However, results of congener specific analysis allowed us to examine the relationship between individual congeners and egg stable isotope values. 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 (10,11). 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. (11)) will be metabolized and eliminated much more rapidly than congeners that lack this structure (Groups I, II, 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 (9). Therefore, we expected that the concentrations of the 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 also expected 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) exhibited a significant relationship with egg isotope values. In contrast, concentrations of congeners with different chlorine substitution patterns (Groups II, III, and particularly I) were rarely correlated with stable isotope values. The relationships that were observed between metabolized PCB congeners 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 (5). Increased rates of PCB decline in Lake Erie herring gull eggs in more recent years probably do not reflect changes in environmental loadings but instead reflect changes in exposure mediated through shifts in diet composition. 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 foodweb structure.

Acknowledgments
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