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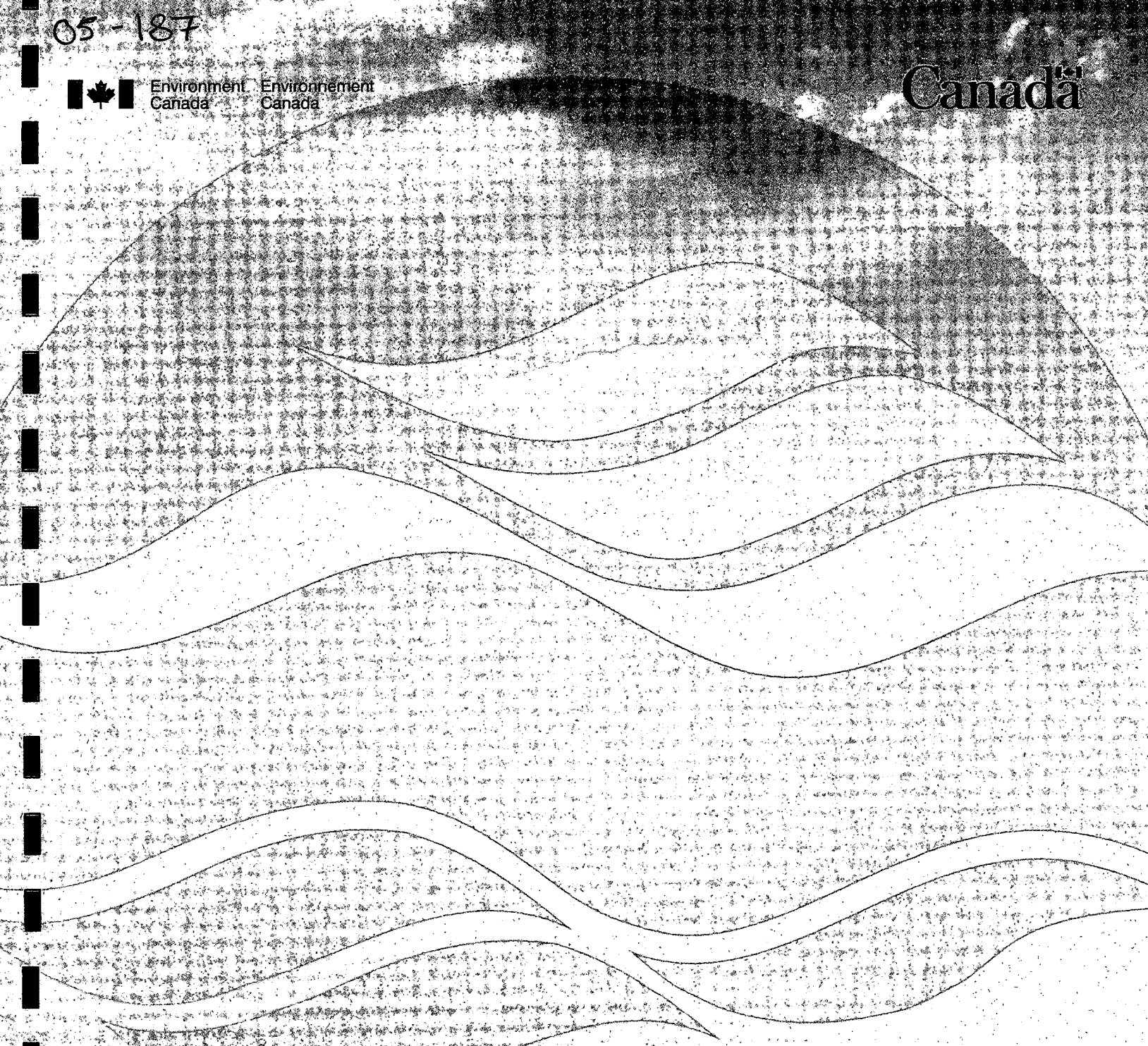

Ecological Tracers Can Quantify Food Web Structure and Change

BY:

C. Hebert, M. Arts, D. Chip Weseloh

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CRAIG E. HEBERT, MICHAEL T. ARTS, D.V. CHIP WESELOH

ABSTRACT

Disruption of natural food webs is becoming a commonplace occurrence as a result of human activities. Harvesting of natural resources (e.g. fishing), climate change, and the introduction of exotic species are but a few of the processes that can significantly alter food web structure and function. It is within this rapidly changing ecological context that we must improve our ability to define food web structure as well as detect and understand the implications of food web change. To do so 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 to provide such information in a predatory seabird, the herring gull (*Larus argentatus*). Stable nitrogen isotopes and fatty acids are used to define diet composition and to determine how diet is affected by ecosystem processes and change. The use of these tracers in concert leads to a better understanding of pathways of energy flow in food webs.

NWRI RESEARCH SUMMARY

Plain language title

Stable isotopes and fatty acids (lipids) help to corroborate that large scale changes in Great Lakes food web structure have occurred

What is the problem and what do scientists already know about it?

In the early 1970s, a long-term monitoring program on the Great Lakes was set up by the Canadian Wildlife Service in conjunction with the International Joint Commission to better understand the effects of prolonged exposure of Herring Gull (*Larus argentatus*) populations to persistent toxic chemicals. There are presently 20,000+ eggs stored, frozen, in this collection. Herring Gull eggs were used because the fat-soluble contaminants are transferred from the female parent to the egg yolk. The monitoring program showed that the levels of most contaminants had declined by up to 90 percent or more by 1995. However, low levels of dioxins, PCBs and other related chemicals are still present in the Great Lakes due to undetected sources, atmospheric deposition, and release from contaminated bottom sediments. In addition, new chemical threats, such as brominated flame retardants, are emerging.

Why did NWRI do this study?

Harvesting of natural resources (e.g. fishing), climate change, and the introduction of exotic species are but a few of the processes that can significantly alter food web structure and function and consequently the flow of contaminants in aquatic food webs. This joint CWS-EC project, which started ~1.5 years ago, aims to showcase how fatty acids (lipids) and stable isotopes in herring gull eggs can be used to detect and quantify long term ecosystem changes in the Great Lakes and also to reveal the inter-relationship between contaminants and certain, key, bioindicator fatty acids.

What were the results?

There has been a shift in the diet of herring gulls in eastern Lake Erie. Since the 1980's smelt (a principal source of fish food and contaminants) has declined. We were able to demonstrate that fatty acids and stable isotopes were mutually complimentary and independently reinforced the concept of wide-scale historical changes in the feeding regime of herring gulls.

How will these results be used?

Detecting and quantifying changes in food web interactions is crucial for properly interpreting wildlife monitoring data relevant to the Great Lakes Monitoring Program and interpreting contaminant data in the correct ecological context.

Who were our main partners in the study?

Canadian Wildlife Service, International Joint Commission

Des traceurs écologiques peuvent quantifier la structure et la modification du réseau alimentaire

CRAIG E. HEBERT, MICHAEL T. ARTS, D.V. CHIP WESELOH

RÉSUMÉ

La perturbation des réseaux alimentaires naturels est devenue chose courante en raison de l'activité humaine. L'exploitation des ressources naturelles (p. ex. la pêche), le changement climatique et l'introduction d'espèces exotiques ne sont que quelques exemples de processus qui peuvent altérer de façon importante la structure et la fonction du réseau alimentaire. C'est dans ce contexte écologique en évolution rapide que nous devons améliorer notre habileté à définir la structure du réseau alimentaire ainsi qu'à déceler et à comprendre les incidences de la modification de celui-ci. Il faut pour cela élaborer, valider et mettre en oeuvre des traceurs écologiques susceptibles de fournir des indications sur le transfert d'énergie, les nutriments et les contaminants dans les réseaux alimentaires. Dans la présente étude, nous examinons l'utilité de deux groupes de traceurs intrinsèques d'origine naturelle dans l'obtention de telles indications chez un oiseau prédateur, le Goéland argenté (*larus argentus*). Des isotopes stables d'azote et des acides gras sont utilisés pour déterminer le régime alimentaire et l'incidence du processus et du changement écosystémiques sur ce dernier. L'utilisation concertée de ces traceurs mène à une meilleure compréhension des véhicules de transfert d'énergie dans les réseaux alimentaires.

Sommaire des recherches de l'INRE

Titre en langage clair

Des isotopes stables et des acides gras (lipides) sont utilisés pour démontrer que des changements de grande portée sont survenus dans la structure du réseau alimentaire des Grands Lacs.

Quel est le problème et que savent les chercheurs à ce sujet?

Au début des années 1970, le Service canadien de la faune a lancé, en collaboration avec la Commission mixte internationale, un programme de surveillance à long terme dans les Grands Lacs visant à mieux comprendre les effets associés à une exposition prolongée à des produits chimiques toxiques rémanents chez des populations de Goélands argentés (*Larus argentatus*). Actuellement, plus de 20 000 œufs provenant de ces populations sont conservés congelés. Les œufs des Goélands argentés ont été utilisés parce que dans le cas de cette espèce les contaminants liposolubles sont transférés des femelles à la graisse nécessaire pour produire le jaune d'oeuf. Le programme de surveillance a démontré que les niveaux de la plupart des contaminants ont diminué jusqu'à 90 % ou plus en 1995. Cependant, de bas niveaux de dioxine, de PCB et d'autres produits chimiques connexes sont encore présents dans les Grands Lacs en raison de l'existence de sources non décelées, de dépôts atmosphériques et de la remise en suspension de sédiments de fond contaminés. En outre, de nouvelles menaces chimiques, comme les produits bromés ignifuges, ont fait leur apparition.

Pourquoi l'INRE a-t-il effectué cette étude?

L'exploitation des ressources naturelles (p. ex. la pêche), le changement climatique et l'introduction d'espèces exotiques ne sont que quelques exemples de processus qui peuvent altérer de façon importante la structure et la fonction du réseau alimentaire et, par conséquent, le flux de contaminants dans les réseaux alimentaires aquatiques. Ce projet conjoint du SCF-EC, lancé il y a un an et demi environ, vise à démontrer comment les acides gras (lipides) et les isotopes stables dans les œufs de Goélands argentés peuvent être utilisés pour déceler et quantifier les modifications de l'écosystème à long terme dans les Grands Lacs et pour révéler également l'interdépendance entre les contaminants et certains acides gras clés bioindicateurs.

Quels sont les résultats?

À l'est du lac Érié, on note un changement dans le régime alimentaire des Goélands argentés. Depuis les années 1980, la population d'éperlan (un des principaux aliments et contaminants pour les animaux aquatiques) a diminué. Nous avons été en mesure de démontrer que les acides gras et les isotopes stables étaient complémentaires et renforçaient de façon indépendante le concept des changements historiques à grande échelle du régime alimentaire des Goélands argentés.

Comment ces résultats seront-ils utilisés?

Déceler et quantifier les changements dans les interactions du réseau alimentaire est primordial pour interpréter correctement les données sur la surveillance des animaux sauvages dans le cadre du Programme de surveillance des Grands Lacs et pour interpréter les données sur les contaminants dans le bon contexte écologique.

Quels étaient nos principaux partenaires dans cette étude?

Service canadien de la faune, Commission internationale mixte.

Ecological Tracers Can Quantify Food Web Structure and Change

CRAIG E. HEBERT[1*], MICHAEL T. ARTS[2], D.V. CHIP WESELOH[3]

[1]Environment Canada, Canadian Wildlife Service, National Wildlife Research Centre, 1125 Colonel By Drive, Ottawa, Ontario, K1A 0H3, Canada
[2]Environment Canada, National Water Research Institute, Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ontario, L7R 4A6, Canada
[3]Environment Canada, Canadian Wildlife Service, Ontario Region, 4905 Dufferin Street, Downsview, Ontario, M3H 5T4, Canada

* Corresponding author phone: (613) 998-6693; fax (613) 998-0458; e-mail: craig.hebert@ec.gc.ca
Author e-mail addresses: M.T.A.: michael.arts@ec.gc.ca; D.V.C.W.: chip.weseloh@ec.gc.ca

Disruption of natural food webs is becoming a commonplace occurrence as a result of human activities. Harvesting of natural resources (e.g. fishing), climate change, and the introduction of exotic species are but a few of the processes that can significantly alter food web structure and function. It is within this rapidly changing ecological context that we must improve our ability to define food web structure as well as detect and understand the implications of food web change. To do so 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 to provide such information in a predatory seabird, the herring gull (*Larus argentatus*). Stable nitrogen isotopes and fatty acids are used to define diet composition and to determine how diet is affected by ecosystem processes and change. The use of these tracers in concert leads to a better understanding of pathways of energy flow in food webs.

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.

Subtle long-term 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 through the detailed examination of the "trophic niche" of a species that is acting as an integrator of food web processes. Trophic niche, in this context, describes diet composition and its effects on trophic position. High trophic level species are useful in this regard as their trophic niche will integrate those processes which, at lower trophic levels, alter prey species abundance and/or consumption. Reconstructing food web dynamics through the use of integrator species can be accomplished through the analysis of archived samples using ecological tracers. 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 "trophic niche" 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) *1000) values in egg protein were found to be 3.4‰ greater than those in the laying female's diet.

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 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 this group has 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. 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: 1) spatial differences in Great Lakes food web structure. We hypothesized that using ecological tracers it would be possible to detect differences in the "trophic niche" of herring gulls from each of the Great Lakes and link these differences to food web processes and 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 Lake Erie food web change. 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*).

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) (Fig. 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).

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 3 times by grinding freeze-dried tissue in (2:1 vol:vol) chloroform:methanol (*26*) and centrifuged at 4000 r.p.m. (4°C) 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 Sartorious 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 #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 #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 x 0.25 mm ID x 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. Three individual pure FA standards (20:2, 20:5n-3, and 22:6n3), were used to estimate the derivitization efficiency (0=~76%). A 37-component FAME standard (Supelco #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. 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 the herring gull's trophic niche at each colony during the 1982-2004 period.

Because of inter-lake differences in baseline $\delta^{15}N$ signatures (see *24*) it was not valid to compare raw $\delta^{15}N$ egg values among lakes. Instead, egg $\delta^{15}N$ 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 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, pers. comm.). $\delta^{15}N_{fish}$ 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 *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 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 validated the use of samples stored at -40°C 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, $F_{14,59} = 4.11$, $p < 0.001$). Mean trophic position estimates for individual colonies ranged from 3.25 at Snake Island in Lake Ontario to 4.14 in the Niagara River (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, $F_{14,59} = 3.51$, $p < 0.001$) and in levels of the individual fatty acids EPA (ANOVA, $F_{14,59} = 3.67$, $p < 0.001$) and DPA (ANOVA, $F_{14,59} = 3.82$, $p < 0.001$). Total n-3 fatty acids showed marginally non-significant 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).

Estimates of gull trophic position and egg n-3/n-6 fatty acid ratios were correlated (Fig 2a). Gull trophic position was also correlated with EPA (Fig 2b) and total n-3 fatty acid ($r = 0.59$, $p = 0.02$) concentrations in eggs. Egg DPA concentrations and trophic position showed a marginally non-significant correlation ($r = 0.48$, $p = 0.07$).

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 likely occupy higher trophic levels than 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 levels of these fatty acids likely reflected greater fish consumption at those colonies. Through the use of stable nitrogen isotope 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*). It is evident that the degree to which fish are consumed is a 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 $\delta^{15}N$ 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 $\delta^{15}N$ 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 $\delta^{15}N$ values from eastern Lake Erie ($r = -0.73$, $p = 0.001$) (Fig 3). In addition, egg $\delta^{15}N$ values were positively correlated with egg EPA concentrations ($r = 0.72$, $p = 0.001$) (Fig 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 $\delta^{15}N$ values ($r = 0.74$, $p = 0.001$) (Fig 5). There were no correlations between egg $\delta^{15}N$ values and concentrations of total n-6, total saturated, total monounsaturated, or total PUFA concentrations. These results indicate that, in years when gulls 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 are correlated with changes in diet composition. In years when more aquatic food was 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 (*33*). The re-direction 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. 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 to high trophic levels. 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 contaminant bioavailability in the Great Lakes (see *34*). 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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Table 1 – Inter-colony differences in mean values of endpoints measured in herring gull eggs collected in 1982, 1987, 1992, 1997, and 2004. 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.

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	3.61^{abc}	0.58^{ab}	1.43^{abcd}	1.29^{ab}	14.41^{a}
3. Gull	Michigan	3.90^{abc}	0.69^{a}	2.17^{a}	1.83^{a}	17.40^{a}
4. Big Sister	Michigan	3.93^{abc}	0.61^{ab}	1.63^{abc}	1.41^{ab}	14.23^{a}
5. Double	Huron	3.77^{abc}	0.58^{ab}	1.52^{abcd}	1.50^{ab}	15.84^{a}
6. Chantry	Huron	3.39^{abc}	0.50^{ab}	1.16^{bcd}	1.27^{ab}	13.01^{a}
7. Channel-Shelter	Huron	3.60^{abc}	0.57^{ab}	1.46^{abcd}	1.46^{ab}	15.17^{a}
8. Fighting	Detroit R.	3.27^{c}	0.56^{ab}	1.14^{bcd}	1.67^{ab}	15.17^{a}
9. Middle	Erie	4.12^{ab}	0.69^{a}	1.87^{abc}	1.90^{a}	15.42^{a}
10. Port Colborne	Erie	4.05^{abc}	0.56^{ab}	1.68^{abc}	1.29^{ab}	15.91^{a}
11. Niagara	Niagara R.	4.14^{a}	0.68^{a}	1.97^{ab}	1.22^{ab}	14.71^{a}
12. Hamilton	Ontario	3.25^{c}	0.59^{ab}	1.59^{abcd}	1.31^{ab}	14.75^{a}
13. Toronto	Ontario	3.38^{abc}	0.49^{ab}	0.97^{cd}	0.94^{b}	12.05^{a}
14. Snake	Ontario	3.25^{c}	0.52^{ab}	1.16^{bcd}	1.01^{b}	13.14^{a}
15. Strachan	St. Lawrence R.	3.27^{ab}	0.41^{c}	0.56^{d}	0.95^{b}	11.75^{a}

Figure Captions

Figure 1 – Location of herring gull monitoring colonies.

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 levels of eicosapentaenoic acid (EPA) in gull eggs. Mean 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 on Figure 1.

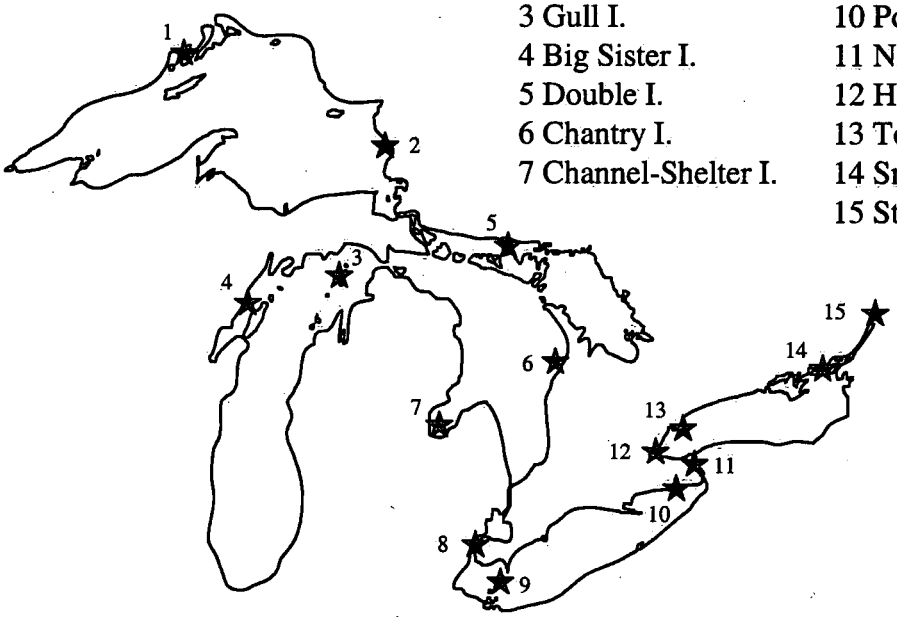
Figure 3 – Temporal trends in egg $\delta^{15}N$ values from Port Colborne, eastern Lake Erie.

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

Figure 5 – Relationship between egg n-3/n-6 fatty acid ratios and egg $\delta^{15}N$ values. Higher n-3/n-6 fatty acid ratios are found in aquatic foods.

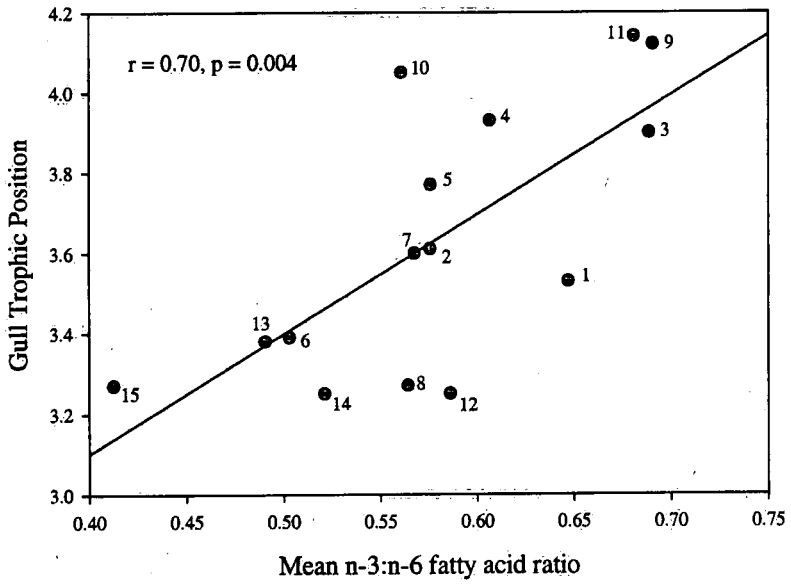
1

Figure 1



1 Granite I.
2 Agawa Rks.
3 Gull I.
4 Big Sister I.
5 Double I.
6 Chantry I.
7 Channel-Shelter I.
8 Fighting I.
9 Middle I.
10 Port Colborne
11 Niagara R.
12 Hamilton Hrbr.
13 Toronto Hrbr.
14 Snake I.
15 Strachan I.

Figure 2


r = 0.70, p = 0.004
Gull Trophic Position
Mean n-3:n-6 fatty acid ratio
4.2
4.0
3.8
3.6
3.4
3.2
3.0
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
11
9
10
4
3
5
7
2
1
13
6
15
14
8
12

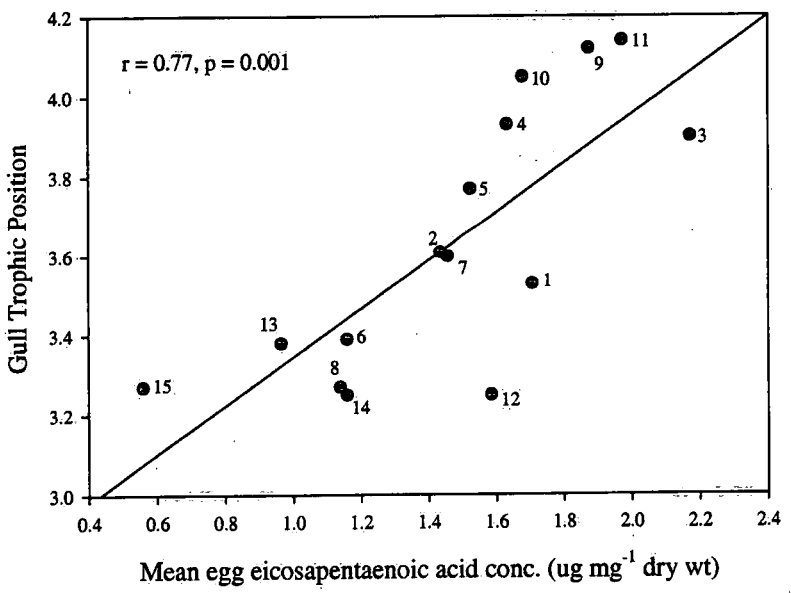

r = 0.77, p = 0.001
Gull Trophic Position
Mean egg eicosapentaenoic acid conc. (ug mg-1 dry wt)
4.2
4.0
3.8
3.6
3.4
3.2
3.0
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
11
9
10
4
3
5
2
7
1
13
6
8
15
14
12

Figure 3

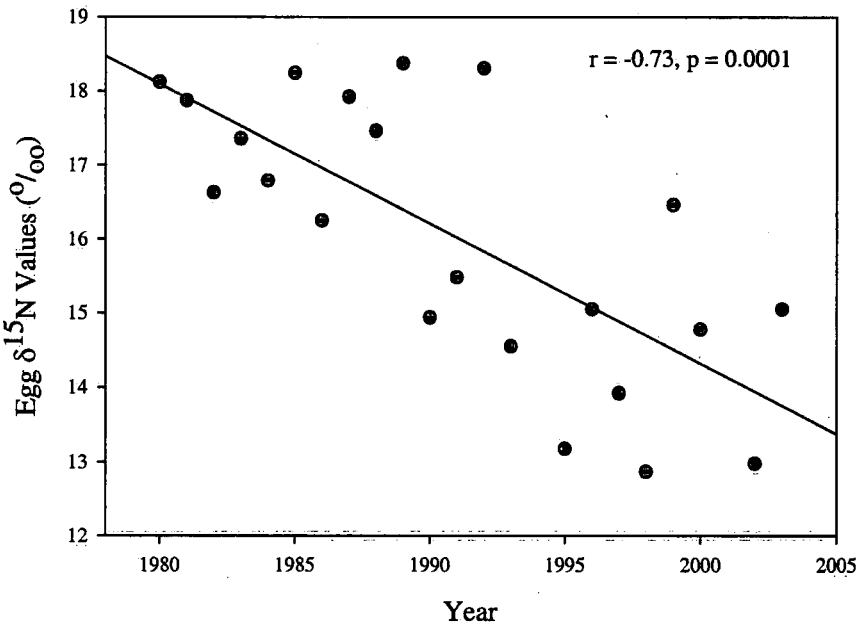

r = -0.73, p = 0.0001
Egg $\delta^{15}N$ Values ($^{o}/_{oo}$)
Year
19
18
17
16
15
14
13
12
1980
1985
1990
1995
2000
2005

Figure 4

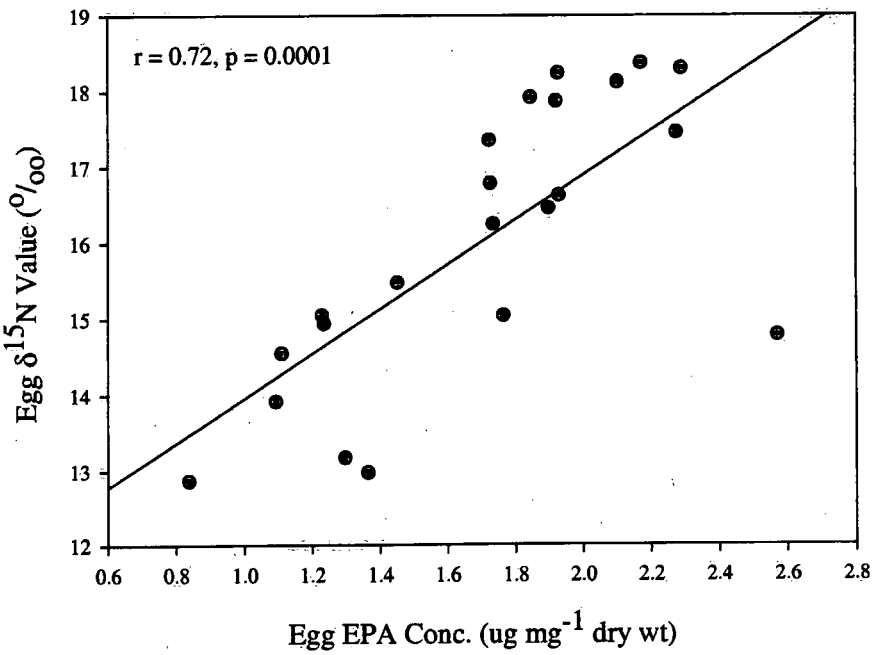
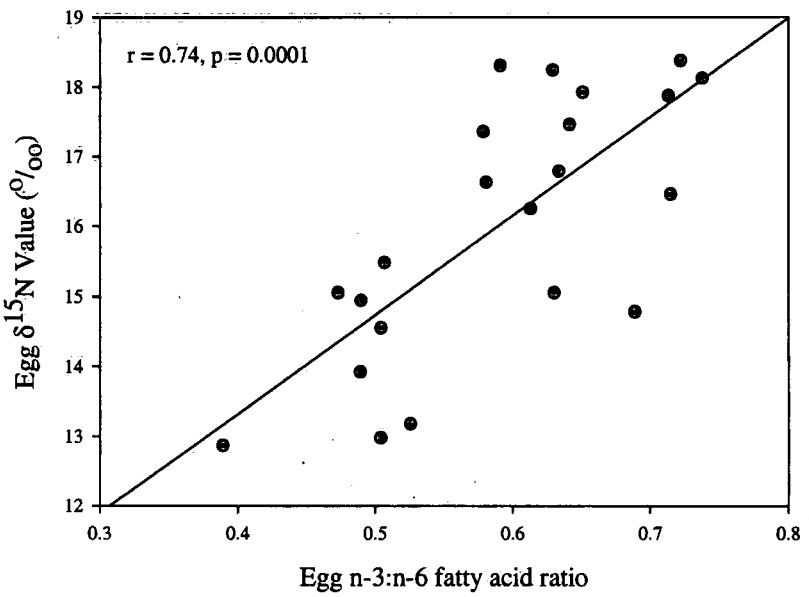

r = 0.72, p = 0.0001
Egg δ15N Value (o/oo)
Egg EPA Conc. (ug mg-1 dry wt)
19
18
17
16
15
14
13
12
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8

Figure5


r = 0.74, p = 0.0001
Egg δ15N Value (o/oo)
Egg n-3:n-6 fatty acid ratio
19
18
17
16
15
14
13
12
0.3
0.4
0.5
0.6
0.7
0.8

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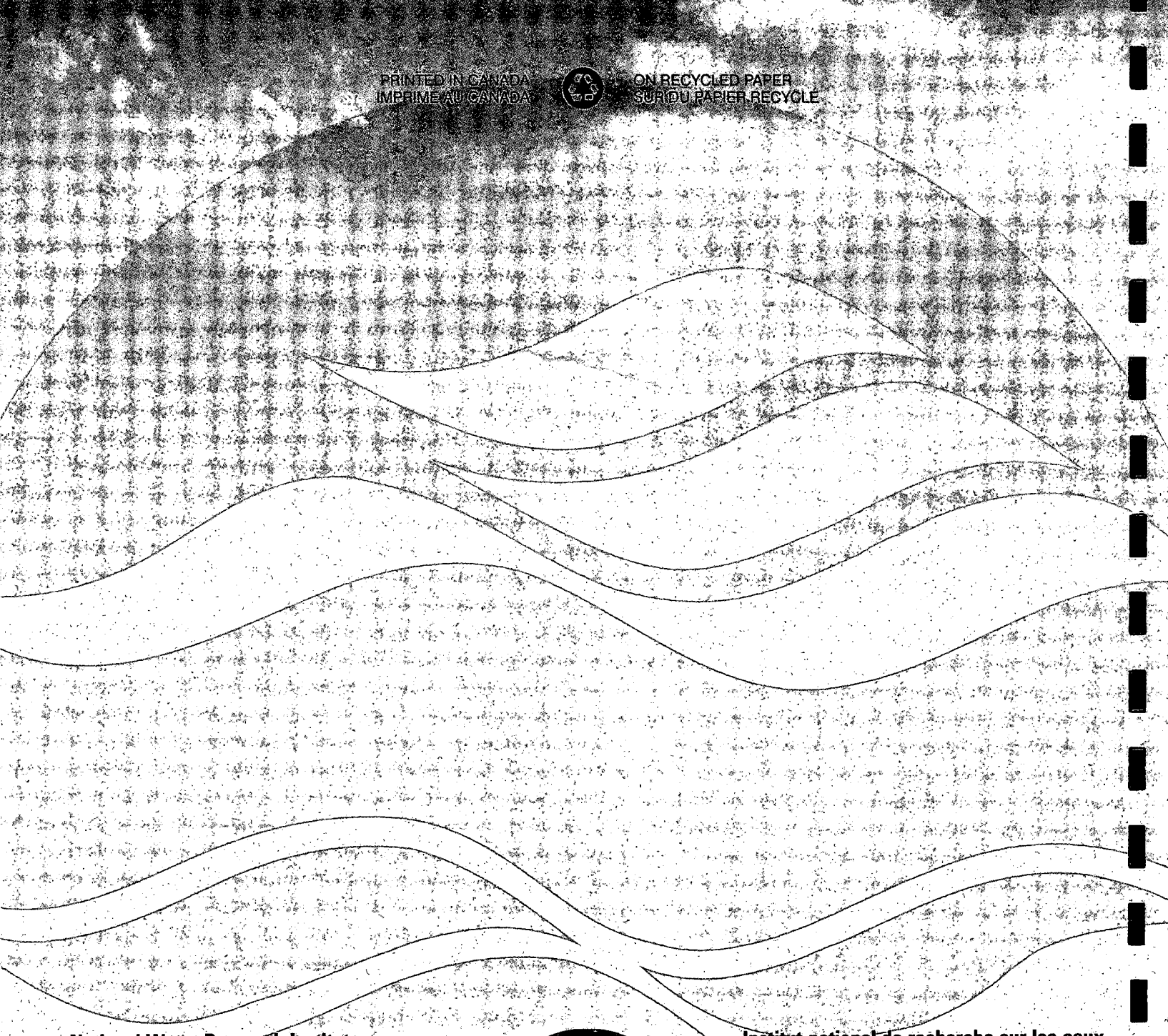

National Water Research Institute
Environment Canada
Canada Centre for Inland Waters
P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

NATIONAL WATER RESEARCH INSTITUTE
INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington, Ontario
L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon, Saskatchewan
S7N 3H5 Canada

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