# University of Windsor Scholarship at UWindsor

**Electronic Theses and Dissertations** 

1995

# Organic contaminants in lower Great Lakes' waterfowl in relation to diet, with particular reference to Dreissena polymorpha.

Edward John. Mazak University of Windsor

Follow this and additional works at: http://scholar.uwindsor.ca/etd

#### **Recommended** Citation

Mazak, Edward John., "Organic contaminants in lower Great Lakes' waterfowl in relation to diet, with particular reference to Dreissena polymorpha." (1995). *Electronic Theses and Dissertations*. Paper 2958.

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.



National Library of Canada Bibliothèque nationale du Canada

Acquisitions and Direction des acquisitions et Bibliographic Services Branch des services bibliographiques

395 Wellington Street Ottawa, Ontano K1A 0N4 395, rue Wellington Ottawa (Ontano) K 1A 0N4

Number - Numerenderskie Our Ness - Numerenderskie

### NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments. La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

AVIS

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

# Canadä

# Organic contaminants in lower Great Lakes' waterfowl in relation to diet, with particular reference to <u>Dreissena polymorpha</u>

by

Edward John Mazak

A Thesis Submitted to the Faculty of Graduate Studies and Research through the Department of Biological Sciences in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario, Canada



National Library of Canada

Acquisitions and Bibliographic Services Branch

395 Weilington Street Ottawa, Ontario K1A 0N4 Biblicthèque nationale du Canada

Direction des acquisitions et des services bibliographiques

395, rue Wellington Ottawa (Ontario) K1A 0N4

Assistile - Volte (efernisce

Our file - Notice reference

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons. L'auteur a accordé une licence irrévocable et non exclusive à la Bibliothèque permettant nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette disposition des thèse à la personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission. L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-10946-1



Edward John Mazak 1995 All Rights Reserved

#### Abstract

Six species of waterfowl including greater scaup (<u>Aythya marila</u>), lesser scaup (<u>Aythya affinis</u>), bufflehead (<u>Bucephala albeola</u>), canvasback (<u>Aythya valisineria</u>), mallard (<u>Anas platyrhynchos</u>), and redhead (<u>Aythya americana</u>) were collected and analyzed for diet content, organic contaminant patterns (pesticides and polychlorinated biphenyls [PCBs]), and stable isotope (<sup>14</sup>C and <sup>15</sup>N) signatures from 3 sites in the lower Great Lakes (Fighting Island, western Lake Erie, and Big Creek). Lesser and greater scaup from Fighting Island were classified into groups according to the percentage dry mass of zebra mussel (<u>Dreissena polymorpha</u>) in the diet. Lesser and greater scaup classified as <u>Dreissena</u>-consumers had, on average, 85 and 67%, respectively, zebra mussel diet content as compared to 6 and 3% for individuals classified as macrophyte-consumers. Other taxa consumed little (6%; bufflehead) or no (0%; canvasback, mallard, redhead) <u>Dreissena</u> at the Fighting Island location. <u>Dreissena</u> was the primary food source of lesser scaup (100%), greater scaup (97%), and bufflehead (72%) in western Lake Erie.

Stable isotope analyses revealed that '<u>Dreissena</u>-consumer' lesser and greater scaup were enriched 2.9‰ and 2.4‰ in <sup>15</sup>N relative to 'macrophyte-consumer' conspecifics. As well, these 'mussel-consumer' waterfowl had 2.6‰ and 2.3‰ higher <sup>15</sup>N levels relative to <u>Dreissena</u>, their principal prey.

Using chemical octanol-water partition coefficients ( $K_{OW}$ ) a representative group of low- (pentachlorobenzene [QCB], polychlorinated biphenyl [PCB] # 28), mid- (PCBs # 105, 153) and high- (PCBs # 194, 206)  $K_{OW}$  compounds were examined in liver tissues for each group of waterfowl. Two-way ANOVAs on lipidadjusted, log-transformed contaminant values for greater and lesser scaup from Fighting Island revealed significant (p< 0.05) differences with respect to diet for

iv

high-K<sub>ow</sub> (PCBs # 194, 206) compounds, though differences among species were insignificant (p>0.10). In each case, mussel-consumers had elevated concentrations of these compounds relative to individuals that avoided <u>Dreissena</u>. Among <u>Dreissena</u>-consumer species, all six compounds except QCB were present in significantly (p<0.05) higher concentrations in lake individuals. Bufflehead from Lake Erie also had significantly higher concentrations of PCB #153 and high-K<sub>ow</sub> compounds than individuals from Fighting Island. Differences in concentrations of all six compounds in mallard from Fighting Island and Big Creek were insignificant. Concentrations of each compound in Fighting Island

Principal component analysis (PCA) was conducted for duck livers using four each of low-, mid-, and high-K<sub>OW</sub> compounds. PC 1 was determined primarily by high K<sub>OW</sub> compounds (PCBs # 206, 153, 194, 180, 105), whereas PC 2 and PC 3 were respectively determined by low K<sub>OW</sub> compounds QCB and PCB # 28. Waterfowl that consumed mainly <u>Dreissena</u> separated clearly on PC 1 and/or PC 2 from ducks that avoided <u>Dreissena</u>. Fighting Island greater and lesser scaup that consumed mussels exhibited PC 1 and PC 2 scores that were similar to conspecifics from Lake Erie.

Biomagnification factors (BMFs), calculated for 39 organic compounds for mussel-consumer scaup were generally below four. BMFs in lesser scaup tended to be lower than those in greater scaup, possibly owing to consumption of smaller, less contaminated mussels by lesser scaup. BMFs tended to increase with increasing log  $K_{OW}$  above ~5.8.

Results from this study indicate that concentrations of most contaminants biomagnify in waterfowl that consume <u>D</u>. <u>polymorpha</u> as a primary food source. Consequently, zebra mussels may serve as both an energy source and conduit for transfer of persistent organic contaminants to higher trophic levels in the Great

Lakes. However, it is not clear whether consumption of <u>Dreissena</u> portends adverse reproductive effects in Great Lakes waterfowl.

For Fred, whose idealism and spirit will live with me forever.

#### Acknowledgements

Foremost I would like express my sincere gratitude to Dr. Hugh MacIsaac for his support and assistance throughout my endeavour. At appropriate moments Hugh shared invaluable experiences that paralleled those I inevitably encountered.

Collection of waterfowl was aided by Dr. Ray Alisauskas (CWS - Saskatoon), Tom Mayrand, Brian Klingbyle, Gary Penner, and Rich Young. Expertise in waterfowl identification by Norm North (CWS - London) was greatly appreciated. Special thanks to Dr. Rodica Lazar and David Qiu (gas chromatography analyses) and Dr. Ray Hesslein (stable isotope analyses). I would like to thank the following people for genuine discussions concerning this project, Glen Fox (CWS - Hull), Mike Weis, Ron Russell, Doug Haffner, Heather Morrison, Sue Roe, Rob Coulas, Andrew Bially, Roland Rocha, Catherine Tessier, Jack Barclay, Christine Custer, and Tom Custer. I am indebted to all for the advice, insight, and feedback I received.

Finally, an enormous thanks to my parents, Ed and Lyl, who provided support and encouragement. To Shonna, your love and understanding was cherished.

# TABLE OF CONTENTS

ABSTRACT	iv
DEDICATION	vii
ACKNOWLEDGEMENTS	viii
LIST OF TABLES	xi
LIST OF FIGURES	xii

INTRODUCT	ION	1
METHODS		7
	Collection Site Description	7
	Waterfowl Collection	8
	Diet Analysis	8
	Organochlorine Contaminant Analysis	10
	Stable Isotope Analysis	12
	Statistical Analysis	13
	Diet	13
	Organochlorine Contaminants	15
	Stable Isotope	16
RESULTS		17
	Waterfowl Diet	17
	Contaminant Concentrations and Profiles	21
	Principal Component	24
	Stable Isotope	25

## TABLE OF CONTENTS

# (continued)

DISCUSSION		
Waterfowl Predation of Mussels	28	
Contaminant Concentrations	31	
Principal Component	38	
Stable Isotope	39	
Reproductive Issues	41	
SUMMARY		
REFERENCES		
APPENDIX A: Contaminant concentration data		
VITA AUCTORIS		

## List of Tables

Table	Title	<u>Page</u>
1	Waterfowl categorized by site, species, and diet	64
2	Basic descriptors of all collected waterfowl by species and site, including sex, size dimensions, and date collected	65
3	Basic descriptors of all collected waterfowl and contaminan analyzed waterfowl categorized by species, site, and diet including sample size, sex, age, mass, size, and % lipid in liver tissue	
4	Chemical correlations of liver versus wing concentrations	. 68
5	Ratios of QCB, p,p'-DDE, OCS, PCBs # 28, 105, 153, 180, 194, and 206 as compared in different waterfowl categories	. 69
6	Two-way ANOVAs for QCB, PCBs # 28, 105, 153, 194, and 206 concentrations in Fighting Island 'macrophyte-consume and ' <u>Dreissena</u> -consumer' scaup	
7	Two-way ANOVAs for QCB, PCBs # 28, 105, 153, 194 and 206 concentrations in Fighting Island and Lake Erie ' <u>Dreissena</u> -consumer' scaup	71
8	Rotated loadings of component 1, 2, and 3 from a principal component analysis of 12 organochlorine compound concentrations in waterfowl	72
9	Comparison of contaminant level results from this study and others	

# List of Figures

Figure	<u>Title</u> Page
1	Location of waterfowl collection sites 74
2	<u>Dreissena</u> right valve length versus right internal septa length
3	Percentage dry biomass diet composition of Big Creek mallard and Fighting Island mallard, canvasback, and redhead
4	Percentage dry biomass diet composition of bufflehead and common goldeneye from Fighting Island and Lake Erie
5	Percentage dry biomass of macrophyte, snail, and <u>Dreissena</u> in the diet of Fighting Island and Lake Erie lesser scaup 82
6	Percentage dry biomass of macrophyte, snail, and <u>Dreissena</u> in the diet of Fighting Island and Lake Erie greater scaup 84
7	Size class distribution of <u>Dreissena</u> consumed by Lake Erie bufflehead, lesser scaup, and greater scaup
8	Contaminant profiles of Big Creek mallard and Fighting Island mallard, canvasback, and redhead 'macrophyte-consumers'. 88
9	Contaminant profiles of bufflehead from Fighting Island and Lake Erie
10	Contaminant profiles of lesser scaup from Fighting Island and Lake Erie
11	Contaminant profiles of greater scaup from Fighting Island and Lake Erie
12	Contaminant profiles of Dreissena, snail, and macrophyte 96
13	Biomagnification factor versus log K <sub>OW</sub> of contaminants for Lake Erie lesser and greater scaup

# List of Figures

# (continued)

Figure	Title Page
14	Factor score plots (components one and two) for waterfowl from the principal component analysis of twelve contaminant concentrations in liver tissue
15	Mean (± se) $\delta^{13}$ C and $\delta^{15}$ N isotope signatures of Fighting Island and Lake Erie waterfowl and respective prey items 102
16	Relative proportions of PCB congeners in bufflehead, lesser scaup and greater scaup from Fighting Island and Lake Erie. 104
17	Greater scaup migration corridors from their breeding grounds in western Alaska to their wintering areas

#### Introduction

The Laurentian Great Lakes have been subject to species introductions since the onset of European settlement in early 1800s. More than 140 non-indigenous species have successfully established in the basin (Mills et al. 1993). Only 10% of these exotic species have had significant economical and/or ecological impacts (Mills et al. 1993). Zebra mussels (Dreissena polymorpha Pallas), potentially the most damaging invader, were likely introduced from ship ballast water discharged into Lake St. Clair or western Lake Erie in 1985 or 1986 (Hebert et al. 1989; Griffiths et al. 1991). The North American distribution of Dreissena includes much of Green Bay, Saginaw Bay, Lake St. Clair, western Lake Erie, Long Point Bay, and shoreline fringes of Lakes Michigan, Huron, Erie, and Ontario (New York Sea Grant 1994). The Mississippi River from Duluth to New Orleans, as well as the tributary rivers Illinois, Ohio, and Arkansas are also inhabited by populations of D. polymorpha. Other river systems that have been colonized by the mussel are the Tennessee and Cumberland in the south, and the Genesee, Susquehanna, Mohawk, Hudson, and St. Lawrence in the northeast. Numerous small inland lakes of Ontario, Ohio, and Michigan also harbour populations of the mussel. The rapid range expansion demonstrates the tremendous invasive capability of Dreissena.

Zebra mussels are now dominant contributors to benthic biomass in Great Lakes ecosystems including western and central Lake Erie, Lake St. Clair, and Saginaw Bay (Leach 1992; Mackie 1991; Griffiths 1992; Nicholls and Hopkins 1993; Holland 1993; Nalepa 1994). Well-established effects of <u>Dreissena</u> include enhanced water transparency, reduced turbidity, and reduced abundances of phytoplankton, zooplankton, and unionid molluscs (MacIsaac 1996). Less well

known are effects of predators on <u>Dreissena</u> abundance, size structure, and the role of the mussel in contaminant dynamics.

Recent studies have described predation of <u>Dreissena</u> by a host of taxa including crayfish (MacIsaac 1994), fishes (French and Bur 1992; French 1993) and waterfowl (Wormington and Leach 1992; Mitchell and Carlson 1993; Hamilton et al. 1994). Waterfowl appear the most likely candidates to have significant impacts on <u>Dreissena</u> populations both in Europe (Stempniewicz 1974; Suter 1982; Stanczykowska et al. 1990; Bij de Vaate 1991; Cleven and Frenzel 1993) and North America (Hamilton et al. 1994). Stanczykowska et al. (1990) estimated that a guild of 4 molluscivorous waterfowl reduced standing <u>Dreissena</u> biomass by up to 20.2% per year in Lake Zegrzynskie, Poland. Coot (<u>Fulica atra</u>) and common goldeneye (<u>Bucephala clangula</u>) were found primarily in areas of Lake Zegrzynskie supporting <u>Dreissena</u> (Stanczykowska et al. 1990). In the river Rhine, wintering tufted ducks (<u>Aythya fuligula</u>) and coots fed extensively on <u>Dreissena</u>, reducing standing biomass by 97% (Suter 1982). However, mussel colonies quickly restored pre-predation biomass levels during summer months through recolonization and growth.

Waterfowl associated with <u>D. polymorpha</u> on Lake Erie include greater scaup (<u>Aythya marila</u>), lesser scaup (<u>A. affinis</u>), common goldeneye and bufflehead (<u>Bucephala albeola</u>) (Wormington and Leach 1992; Hamilton et al. 1994). Waterfowl have long utilized the north shore of Lake Erie as a staging point during migration. For example, McCullough (1981) reported mixed greater and lesser scaup flocks of up to 39,000 individuals during staging periods near Nanticoke, Ontario. Wormington and Leach (1992) recorded dramatic increases in the number of staging greater and lesser scaup and common goldeneye subsequent to establishment of massive <u>Dreissena</u> populations in the western basin of Lake Erie. Moreover, staging duration for diving ducks appears to have lengthened

following <u>Dreissena</u> establishment (Wormington and Leach 1992; C. Custer pers. comm.). Recent studies indicate that during their stay in the Lake Erie area, ducks may have a significant impact on littoral <u>Dreissena</u> biomass. Hamilton et al. (1994) determined that waterfowl staging during autumn in the Point Pelee, Ontario, area of western Lake Erie consumed 57% of <u>Dreissena</u> biomass in nearshore waters. Waterfowl have also been reported drowned in commercial gill nets deployed in deeper regions of western Lake Erie known to support <u>Dreissena</u>.

Bivalve molluscs are excellent biomonitors of contaminants in marine and estuarine environments. The National Oceanic and Atmospheric Administration's Status and Trends Mussel Watch Program was developed to monitor the current status and long-term trends of chlorinated pesticides, PCBs, polycyclic aromatic hydrocarbons and trace metals in bivalves and sediments along the coasts of the United States of America (Farrington et al. 1983; Sericano et al. 1990). In European freshwater systems, Kraak et al. (1991) and Mersch et al. (1992) employed <u>D</u>. polymorpha as a biomonitor; the mussel provided a time-integrated picture of bioavailable levels of metals and organochlorine compounds exposed to biota. Both research groups identified <u>D</u>. polymorpha as an optimal sentinel organism for biomonitoring. In 1992, NOAA adopted <u>D</u>. polymorpha in their "mussel watch" program to monitor freshwater sites in the Great Lakes. For example, organic contaminants (total PCBs) in zebra mussels from Grosse lle (Detroit River), Put-in-Bay (western Lake Erie), and the Saginaw River were more than one standard deviation above national mean values (Robertson et al. 1993).

Other studies have demonstrated the utility of <u>D</u>. <u>polymorpha</u> as a biomonitor of metal (e.g. Secor et al. 1993; Mersch et al. 1993; Kraak et al. 1994) and organic (e.g. Duursma et al. 1984; Doherty et al. 1993; Fisher et al. 1993; Brieger and Hunter 1993; Marvin et al. 1994) contamination. The species appears particularly

well suited as a biomonitor owing to its rapidly increasing North American distribution, large sedentary populations, and ability to concentrate PCBs to a greater extent than native taxa. For example, Brieger and Hunter (1993) reported that zebra mussels from Lake St. Clair and Lake Erie had higher accumulations of Arochlors 1242 and 1254 than native Lampsilis siliquoidea clams. In addition, Kreis et al. (1991) found that in some cases, total PCB concentrations in zebra mussels were an order of magnitude greater than in native L. radiata from the Huron-Erie corridor. A number of workers have speculated but not demonstrated that <u>Dreissena</u> may serve as a conduit for transfer of contaminants to higher trophic levels (Landrum et al. 1990; Kraak et al. 1991; Kreis et al. 1991).

Little information exists regarding potential biomagnification of organic contaminants in predators that feed on <u>Dreissena</u>. However, de Kock and Bowmer (1993) found that European tufted ducks fed zebra mussels contaminated with a wide array of organic compounds (PCBs, DDE, HCB) laid fewer eggs, abandoned nests more often and had higher embryo and chick mortality rates than ducks fed less polluted mussels. Greater and lesser scaup wintering in Long Island Sound, Connecticut, had high levels of metals and DDT, DDE, and DDD (Barclay and Zingo 1993). These wintering migrant scaup populations of Long Island Sound have been in decline since the 1950's, possibly owing to low breeding success, high juvenile bird mortality, or because juveniles now winter farther west on the Great Lakes (Barclay and Zingo 1993).

Because waterfowl do not bioconcentrate organic contaminants like gilled aquatic organisms, the predominant source of exposure may be through diet or drinking water (Heath et al. 1972; Nebeker et al. 1992). Exposure through dermal contact with water is generally limited by low water solubilities of organic contaminants. Studies investigating accumulation or health effects of organic contaminants in waterfowl rely almost exclusively on spiked diets to administer the

dose (Heath et al. 1972; Custer and Heinz 1980; Haseltine and Prouty 1980; Scholten et al. 1989; de Kock and Bowmer 1993; Nebeker et al. 1994). Accumulation through ingestion depends on the concentration of contaminant in the food source, amount of food consumed, and assimilation efficiency.

Macrophytes can bioconcentrate PCBs 6,000 - 9,000 times the concentration in surrounding water (Painter 1990). However, contaminant concentrations in macrophytes are considerably lower than in <u>Dreissena</u>, which bioconcentrate PCBs up to ~178,000 times levels in water (Landrum et al. 1990). Waterfowl that consume contaminated <u>Dreissena</u> may thus be exposed to higher concentrations of contaminants than individuals that consume macrophytes. Evidence exists from other systems demonstrating elevated concentrations of contaminants in members of 'high' trophic levels (Rasmussen et al. 1990; Russell et al. 1995). Bioaccumulation of PCBs and other organic compounds in a Lake Ontario food chain was found to be higher than that expected by bioconcentration from water alone (Oliver and Niimi 1988). Contaminant data was lipid normalized to account

for increased lipid levels of higher trophic level organisms (salmonids), yet observed bioaccumulation factors were still five times higher than predicted. Biomagnification or uptake from food was implicated in the increased contaminant levels in top fish predators (Oliver and Niimi 1988). As well, highly chlorinated compounds, including hexachlorobiphenyls and heptachlorobiphenyls, comprised a greater proportion of total PCB concentration in high trophic position species.

Stable isotopes have been successfully applied to food chain and contaminant bioaccumulation studies (Peterson and Fry 1987; Keough 1994). For example, in biota from freshwater systems, Cabana and Rasmussen (1994) and Kidd et al. (1995) found strong correlations between measures of stable nitrogen isotope levels and both trophic level and contaminant burden. Typically, there is an increase of 3‰ and 1‰ of  $\delta^{15}$ N and  $\delta^{13}$ C signatures, respectively, with each

increase in trophic level owing to time-integrated isotope assimilation and enrichment over dietary food sources (Peterson and Fry 1987; Hobson and Clark 1992; Hobson et al. 1994).

The purpose of this study is to address whether waterfowl that exploit zebra mussels in the Detroit River and western Lake Erie are exposed to higher levels of organic contaminants than con- or heterospecific individuals with different diets. Specifically, I explore inter- and intraspecific variation in contaminant burden in relation to diet. Because conventional analyses are limited to correlations between present duck diet and contaminant concentration, an accurate picture of exposure may not emerge if, for example, present diet does not reflect past diet nor past contaminant exposure. Thus, in this study, I complement conventional diet and contaminant analyses with those of stable isotopes for waterfowl and putative food sources. The specific hypothesis tested is that body burden and biomagnification of persistent organic compounds is not related to waterfowl diet, species or collection site.

#### Methods

#### Collection Site Descriptions

Watr..iowl were collected from three major sites, Fighting Island (42°11'N 83°07'W) in the lower Detroit River, western Lake Erie between Middle Sister (41°51'N 83°00'W) and Hen Islands (41°47'N 82°47'W) and the north shore, and Big Creek Marsh (42°02'N 83°03'W) (Figure 1). The lower Detroit River has been documented as a major over-wintering site for waterfowl with suitable habitat and food resources (Davis and Erwin 1982). Historically, Fighting Island was a dumping site for Wyandotte Chemical (Michigan). Herring gull eggs from Fighting Island contained among the highest levels of PCBs detected from 25 Great Lakes sites from 1979 to 1982 (Struger et al. 1985). A wetland downstream of Fighting Island is used extensively by migrating and local waterfowl (Prince et al. 1992). Hunting is prohibited in the wetland, which serves as a sanctuary. Nearby shallow areas within the river support extensive beds of aquatic macrophytes, including Vallisneria americana, Elodea canadensis and Potamogeton spp. (Drobney et al. 1982; Prince et al. 1992). Gastropods and <u>Dreissena</u> occur on macrophytes and on mud flats in the area (Drobney et al. 1982; pers. obs.).

Hen Island is located 8 km west of Pelee Island in western Lake Erie. Middle Sister Island is located west of Hen Island, 15.7 km from the Canadian mainland (Colchester, ON) in the central region of the basin. Mean water depth for the basin is 7.6 m, though 8 - 10 m deep passages exist between the islands (Bartish 1987). Commercial fishermen employ gill nets seasonally throughout the western basin of the lake, including in the study area.

#### Waterfowl Collection

121 waterfowl were collected for the study. Individuals from Fighting Island were donated by duck hunters from LaSalle Sportsmen's Club who agreed to participate in the study. Fighting Island taxa collected included mallard, canvasback (Aythya valisineria), bufflehead, redhead (Aythya americana), and greater and lesser scaup. All Fighting Island individuals were collected during autumn 1993 or autumn 1994. Whole carcasses of lake ducks were obtained from commercial fishermen who found individuals entangled and drowned in gill nets at depths up to 7 m. Lake Erie greater and lesser scaup, common goldeneye, and bufflehead were collected between autumn 1993 and December 1994. In addition, on November 12, 1993, a sample of 19 mallards (Anas platyrhynchos) were obtained from Big Creek on the Canadian mainland from hunters affiliated with the Big Creek Hunters Club. Waterfowl species, age and sex were identified according to Carney (1992), and later verified by Norm North of the Canadian Wildlife Service, London, Ontario. Duck mass was determined to the nearest 25 g using a spring balance (Ohaus), wingspan and length measurements were recorded to the nearest 0.5 cm using a measuring tape, digestive tracts were removed for diet analysis, and liver and/or wing tissues were collected for organochlorine contaminant and stable isotope analysis. Although common goldeneye were collected, neither organochlorine nor stable isotope analyses were carried out since only Lake Erie individuals were available in late 1994; thus goldeneye results are limited to diet analysis only.

#### <u>Diet Analysis</u>

Contents of digestive tracts (esophagus, proventriculus and gizzard) excised from ducks were analyzed for all study ducks. Decomposition of food items, particularly in the gizzard, limited taxonomic resolution. Diet contents were

categorized into 4 primary fractions: <u>Dreissena</u>, snail, macrophyte (mainly <u>Elodea</u>, <u>Vallisneria</u>, and <u>Potamogeton</u> spp.) or amphipod. With the aid of a stage micrometer and dissecting microscope (Zeiss), whole mussels obtained from the digestive tracts of all ducks were measured to the nearest 0.01 mm to determine right valve length and right internal septa length (Figure 2). Least squares linear regression of valve length on septa length allowed reconstruction of whole mussel size from shell fragments for which only right septa lengths could be obtained from the gizzard (Olszewski 1978; Hamilton 1992). Diet contents were air dried for at least 72 hours to a constant weight at 20°C and expressed as proportion dry biomass. Diet content dry mass (± 0.0005 g) was determined using an electronic balance (A&D).

While it is possible that the collection methods at different sites (hunting versus gill-net drowning) may have biased diet surveys, this possibility is unlikely considering that all waterfowl were actively engaged in food acquisition when killed or drowned. All hunted ducks were in identified feeding sites when killed, while drowned individuals were often found at considerable depth in areas with <u>Dreissena</u>. In addition, many drowned ducks had zebra mussels in their mouth and esophagus.

When possible, samples of primary diet items of waterfowl were collected fresh from field sites for organochlorine contaminant and stable isotope analysis. Aquatic macrophytes from Fighting Island were collected by hand in 1.5 m of water in August 1994, while snails and zebra mussels were obtained by benthic dredge (mesh size 2 mm) in 1.5 - 2.5 m depth on December 18, 1994. <u>Dreissena</u>, macrophytes and gastropod samples from Middle Sister Island, Lake Erie were collected by SCUBA during September 1994 in 2 - 3 m water.

#### Organochlorine Contaminant Analysis

Excised wing and liver tissues from ducks were immediately wrapped in hexane-rinsed aluminum foil following collection and frozen until analyzed. Sample preparation and gas chromatography methods follow Lazar et al. (1992) and are presented here only briefly. Tissue was dehydrated and prepared by grinding 3 - 5 g of tissue with 20 g of sodium sulfate with the use of mortar and pestle. Prepared tissue mixture was added to 4 g sodium sulfate in a glass-woolplugged 2.1 cm X 33 cm glass column for extraction, and capped with an additional 10 g of sodium sulfate. Just enough hexane was added to submerge the column contents; the column was then allowed to sit for one hour to saturate. 250 mL of dichloromethane/hexane (50/50 solution) was added to the column and eluted through at a 5 - 10 mL minute<sup>-1</sup> rate, collected in a round bottom glass flask, then roto-evaporated to 25 mL. Two mL of this extract was used for lipid determination by oven drying at 105°C. The remaining 23 mL was evaporated to 2 mL, then brought back up to volume by the addition of 5 mL isooctane, then further evaporated to 1 mL. This isooctane carrier was cleaned-up on a 1 cm X 24 cm glass column containing 6 g of activated florisil topped with 2 cm of sodium sulfate. Up to three fractions were collected in evaporating flasks that initially contained 5 mL of isooctane. First, 50 mL of hexane was run through the florisil column at a slow drip and collected as fraction one. The addition of 36 mL 15% dichloromethane/hexane and subsequent collection yielded fraction two. Finally, 52 mL of 50% dichloromethane/hexane was added, and the eluate was considered fraction three. All fractions were evaporated to 2 mL, transferred to a 5 mL volumetric flask and brought up to volume with hexane used to rinse the evaporating flask. Each fraction was run separately on a Hewlett Packard-5890 Gas Chromatography / <sup>63</sup>N-Electron Capture Detector instrument. Canadian Wildlife Service standards were run as references every 6 - 8 samples. PCB

identification numbers and associated log K<sub>OW</sub> values are based on IUPAC classification system (Shiu and Mackay 1986; Hawker and Connell 1988).

Organochlorine contaminant analysis of 65 different compounds was conducted on a total of 52 ducks based on species, site, and diet. Some chemicals were deleted from further analysis owing to coelution properties or because the majority of samples had nondetectable levels (<0.05 µg kg<sup>-1</sup> wet weight), leaving 39 suitable compounds. When more than half of the samples had detectable levels of a particular contaminant, the remaining 'nondetect' values were replaced with random values between 0.00 and 0.05 µg kg<sup>-1</sup> wet weight generated in Quattro Pro.

The percent lipid in liver and wing ranged between 3.3 and 5.7% but did not vary among groups of waterfowl. Wet weight chemical concentrations were lipid normalized.

In a subsample of 11 ducks, both wing and liver tissues were analyzed. Lipidnormalized liver concentrations were regressed on lipid-normalized wing concentrations for these individuals. The R<sup>2</sup> values for all chemicals (39 compounds) were assessed against their respective log K<sub>OW</sub> to determine the relationship between contaminants in wing and liver based on the log K<sub>OW</sub> of the contaminant. Equivalent lipid-adjusted liver concentrations were calculated using the regression equations described above for eight individuals for which only lipid-adjusted wing values were available. R<sup>2</sup> values for the 12 compounds used in statistical models (see below) ranged from 0.72 (QCB and PCB # 28) to 0.99 (PCB # 174 and 180). The number of individuals analyzed for contaminants (sorted by site, species and diet) ranged between 3 and 8.

Biomagnification factors (BMFs) were calculated for greater and lesser scaup from Lake Erie using zebra mussels from Middle Sister Island as a prey reference. Of the mussels that were collected in September 1994, a size distribution similar

to that consumed by waterfowl (determined from previous diet analysis), was selected for organic contaminant analysis. BMFs were calculated as:

BMF = [pred] ÷ [prey] where [pred] and [prey] are respective lipid-normalized concentrations of contaminants in waterfowl predators and <u>Dreissena</u> prey.

#### Stable Isotope Analysis

Stable carbon and nitrogen isotope analysis was carried out on 24 waterfowl wing tissue samples and 9 gut content diet item samples (macrophytes, snails, and <u>Dreissena</u>) collected from the field. The analysis requires that all samples be lipid-free and as dry as possible. Waterfowl sample preparation involved trimming all visible fat off excised wing tissue, and dicing tissue into 5 mm square cubes. Zebra mussels and snails collected from Lake Erie were shucked and the soft tissue diced similarly. Cubes were placed in a glass-stoppered flask and swirled in an acetone suspension (100 mL) for 15 minutes. Cubes were then rinsed with dichloromethane (50 mL) for 1 minute. Tissue was oven dried for 48 - 72 hours at 60°C and powdered with a mortar and pestle. Plant material from Fighting Island was oven dried then powdered in a Wiley Mill. Powdered samples were sent to Department of Fisheries and Oceans, Winnipeg, for analysis in conjunction with Canada Centre for Inland Waters, Burlington. Analysis followed a modified Dumas automated combustion, continuous flow method (Fiesslein et al. 1989; Fry et al. 1992). Samples (~20 mg) are combusted to gases at 850°C for 2 h in a sealed Vycor tube with 1 g copper wire, 1 g copper oxide, and a 1 mm<sup>2</sup> piece of silver foil. High temperature will fully oxidize the sample to gaseous CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O. Oxides of nitrogen are reduced over copper. Cold vapour traps allow cryogenic separation of the gases based on differential volatilization. The sample gas enters a dual-inlet isotope ratio mass spectrometer (VG Micromass 602E) and

run against standards for separate determination of  $\delta^{13}$ C and  $\delta^{15}$ N values. The del ( $\delta$ ) notation represents parts per thousand ( $\infty$ ) or the ratio of the heavier isotope to the lighter isotope in the sample relative to the standard:

$$\delta X = \left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000$$

where X is <sup>13</sup>C or <sup>15</sup>N and R is the corresponding ratio <sup>13</sup>C:<sup>12</sup>C or <sup>15</sup>N:<sup>14</sup>N. Peedee belemnite and atmospheric nitrogen were used as standards for <sup>13</sup>C and <sup>15</sup>N, respectively (Peterson and Fry 1987).

Typically <sup>13</sup>C and <sup>15</sup>N are enriched approximately 0 - 1‰ and 3 - 5‰ respectively per trophic level (Peterson and Fry 1987; Hamilton et al. 1992; Cabana and Rasmussen 1994; Keough 1994). When combined with isotope profiles of food sources (macrophytes, snail, <u>Dreissena</u>), it may be possible to assess long-term assimilation patterns in waterfowl in relation to patterns in putative food sources (e.g. see Hobson et al. 1994).

#### Statistical Analysis

#### <u>Diet</u>

Preliminary diet analysis revealed that Fighting Island waterfowl consumed either mussels as a majority component of the diet and were termed 'musselconsumer', or foraged mainly on macrophytes and were classified as 'macrophyte-consumers'. Waterfowl diet comparisons were conducted using ANOVAs and t-tests on arcsine square root-transformed proportions of plant, snail, <u>Dreissena</u>, or amphipod dry mass in the diet. ANOVAs were performed to detect diet differences on the following sets of waterfowl that were used in contaminant analysis (Table 1). First, the proportion zebra mussel, snail or amphipod in Lake Erie bufflehead, lesser scaup, and greater scaup were compared using separate

ANOVAs. In order to justify 'mussel' and 'macrophyte' diet classifications, a 2-way ANOVA was conducted on proportion <u>Dreissena</u> in the diet of Fighting Island lesser and greater scaup that were classified into 'mussel-consumer' or 'macrophyte-consumer' groups; similarly, separate tests were conducted using proportion macrophyte and snail. Next, the proportion of plant in the diet of all Fighting Island plant-consumer waterfowl (mallard, redhead, canvasback, bufflehead, and 'macrophyte-consumer' lesser and greater scaup) were analyzed by ANOVA. Additionally, a 2-way ANOVA was carried out on the proportion on zebra mussels in the diet of Fighting Island lesser and greater scaup 'musselconsumers' versus Lake Erie lesser and greater scaup 'mussel-consumers' to determine if consumption of <u>Dreissena</u> was comparable across species and sites.

Student's t-tests were performed on transformed proportion <u>Dreissena</u>, macrophyte, snail and amphipod in diets of Lake Erie and Fighting Island bufflehead to determine whether diet preferences differed between sites. As well, a Student's t-test was conducted on the proportion plant in Fighting Island and Big Creek mallard to determine whether diets were similar at each site. The level of significance was set at 5% (Systat 1992).

Also, diet comparisons between GC analyzed and non-GC analyzed waterfowl were made to assess whether individuals selected for GC analysis had diets similar to or typical of additional waterfowl that were collected. Therefore, Student's t-tests were carried out on gas chromatography contaminant analyzed waterfowl and other non-GC analyzed waterfowl using transformed diet data for respective waterfowl of all groups (by site, species, and consumer type; see Table 1).

Size distributions of mussels consumed were compared statistically using Kolmogorov-Smirnov tests for all combinations of Lake Erie bufflehead, lesser scaup and greater scaup, using an adjusted probability of  $\alpha = 0.016$  (.05/3).

#### Organochlorine Contaminants

Analysis of differences in contaminant concentrations were limited to a group of four low-K<sub>OW</sub> (HCB, OCS, QCB, PCB # 28), mid-K<sub>OW</sub> (PCBs # 105, 118, 149, 153) and high-K<sub>OW</sub> (PCBs # 174, 180, 194, 206) compounds. These compounds were selected because, within each category, they had the lowest correlations between chemicals ( $R^2$ =0.46 to 0.91). As well, I attempted to use compounds that are frequently utilized in published studies. However, substitution of other compounds for the ones included here had no material effect on results (pers. obs.). Although many comparisons were possible to test for diet effects on contaminant burdens, I have limited most analyses to greater and lesser scaup collected at Fighting Island and Lake Erie. A two-way ANOVA was conducted using lipid-normalized, log(x+1)-transformed chemical concentration data to assess species and diet effects. Tests were repeated for each of QCB and PCBs # 28, 105, 153, 194 and 206 (i.e. two low-, mid- and high-K<sub>OW</sub> compounds as log K<sub>OW</sub> representatives).

Location effects (Lake Erie versus Fighting Island) were also analyzed using 2-way ANOVA and 'mussel-consumer' greater and lesser scaup from the two sites. Location effects were also analyzed, separately, using t-tests (with adjusted  $\alpha$ =0.0085) on bufflehead from Lake Erie and Fighting Island, and also mallard from Big Creek and Fighting Island. The former analysis involving bufflehead is, however, confounded by diet differences between sites. Contaminant levels in <u>Dreissena</u> from Fighting Island and Lake Erie were also compared by t-test.

Biomagnification factors for Lake Erie lesser and greater scaup were regressed on log K<sub>OW</sub> for a select class of compounds. Compounds included in this analysis were limited to 33 PCBs exclusive of QCB, HCB, dieldrin, DDE, OCS, and mirex. Analysis of covariance was used to assess the relationship of biomagnification factor and chemical log K<sub>OW</sub> in lesser and greater scaup.

Principal component analysis (PCA) was conducted for the 12 organochlorine compounds described above. Data were lipid-adjusted and log(x+1)-transformed prior to analysis. The model employed a correlation matrix and varimax rotation to generate principal components (Systat 1992). Compounds that loaded greater than 0.70 on a component were regarded as significant in determining that component. Variables that simultaneously loaded > 0.30 on more than one component were complex variables and were not considered important in determining components. Variable loadings were used to determine scores for individual ducks which were then plotted to display associations between groups of waterfowl in two major principal component dimensions. Mean waterfowl factor scores on Principal Component (PC) 1 and PC 2 were analyzed using two-way ANOVAs to assess diet and location effects. One-way ANOVA was used to assess differences in factor scores for all ducks from Fighting Island that avoided <u>Dreissena</u>; Scheffé's multiple comparisons test was used to identify waterfowl with significantly different mean PCA scores (Day and Quinn 1989).

#### Stable Isotope

Carbon and nitrogen signatures in Fighting Island and Lake Erie scaup (greater and lesser) were subject to a multivariate-ANOVA in order to compare the effects of species and diet. To include all species, stable isotope data for <sup>13</sup>C and <sup>15</sup>N were analyzed separately using two way ANOVAs (diet and species) to compare whether 'mussel-consumer' waterfowl were enriched in <sup>13</sup>C and <sup>15</sup>N over 'macrophyte-consumer' waterfowl and whether any species differences were evident. Finally, 1-way ANOVAs with post hoc Dunnett's one sided tests were run separately for carbon and nitrogen on all species of waterfowl compared to their respective food source (Systat 1992). Separate tests were conducted on Fighting Island and Lake Erie food chains.

#### Results

A total 121 ducks were collected for this study, all of which were in fine physical shape and appeared healthy. Only one duck, a common goldeneye collected from Lake Erie, was discovered with a grossly visible tumour (1 cm dia.) located on the intestine. Overall the sample contained 47% female and 53% male individuals, of which 55% were hatching-year juveniles and 45% adults. Mallard drakes comprised the majority of the Big Creek sample; hatching-year females were most commonly collected at both Fighting Island and Lake Erie (Table 2). Big Creek mallard were the largest and heaviest ducks, while bufflehead from Lake Erie were the smallest and lightest ducks studied. Lesser and greater scaup from Lake Erie were slightly larger and heavier than conspecifics from Fighting Island (Table 2). Over half of the waterfowl in this study were obtained in the month of November.

Mean ( $\pm$  1 standard error) lipid levels for GC analyzed waterfowl were 4.4%  $\pm$  2.3. Lipid levels did not vary significantly by species or diet (3-way ANOVA, p>0.10) and insignificant differences were found by site (F=2.82, df=2,43, p=0.07). GC analyzed waterfowl were representative of total waterfowl collected with respect to mass and size (Table 3).

#### Waterfowl Diet

Diets of mallard and redhead from Fighting Island and mallard from Big Creek consisted of macrophytes only (Figure 3). Canvasback diets consisted of >94% macrophytes, with a small component of snail (Figure 3). Bufflehead from Fighting Island also consumed primarily macrophytes (80%), and only small amounts of snail (12%) and <u>Dreissena</u> (8%) (Figure 4). This pattern was reversed in western Lake Erie, where bufflehead consumed 72% <u>Dreissena</u>, 26% amphipod, 2% snail

and no macrophytes. Lake Erie bufflehead consumed a significantly greater proportion of <u>Dreissena</u> (Student's t-test, t=6.78, p<0.01) than Fighting Island individuals. However, the two groups had insignificant differences in the proportion of snail consumed (t=2.18, p=0.0654). Only bufflehead from Lake Erie consumed amphipod, while only Fighting Island individuals consumed macrophytes. Common goldeneye whether collected from Fighting Island or Lake Erie had consumed over 83% <u>Dreissena</u> (Figure 4). Lake Erie common goldeneye utilized 15% amphipod.

Lake Erie lesser and greater scaup consumed primarily or exclusively <u>Dreissena</u> (Figures 5, 6). By contrast, individuals from Fighting Island could be divided into those that ate either mainly <u>Dreissena</u> or mainly macrophyte (Figures 5, 6).

The three species of Lake Erie birds, bufflehead, lesser scaup, and greater scaup, differed significantly in the proportion of zebra mussel in the diet (1-way ANOVA, F=74.22, df=2,15, p<0.01). Bufflehead consumed a significantly lower (72%) proportion <u>Dreissena</u> than greater scaup (97%), which in turn consumed significantly less <u>Dreissena</u> than lesser scaup (100%) (Scheffé's test,  $\alpha$ =0.05). The three species also differed in the proportion of snail ingested (ANOVA, F=8.48, df=2,15, p<0.01). The proportion of snail did not differ among bufflehead (2.4%) and greater scaup (3.2%), though lesser scaup (0%) differed significantly from the other two (Scheffé's test,  $\alpha$ =0.05). Additionally, the proportion of amphipod in diet differed among the three species (ANOVA, F=221.05, df=2,15, p<0.01), being significantly higher in bufflehead (26%) than in lesser scaup (0%) and greater scaup (0%) (Scheffé's test,  $\alpha$ =0.01).

Considering Fighting Island lesser and greater scaup only, 'musselconsumers' (85% and 67%) consumed significantly more <u>Dreissena</u> than 'macrophyte-consumers' (6% and 3%) (2-way ANOVA, F=118.20, df=1,10,

p<0.01), though differences among species were not evident (F=2.21, df=1,10, p>0.10). As well, the species\*diet interaction was not significant (F=1.42, df=1,10, p>0.10). Similarly, 'mussel-consumer' ducks consumed significantly less plant (2-way ANOVA, F=16.00, df=1,10, p<0.01) than 'macrophyte-consumers'; the species and species\*diet interaction were insignificant (F=0.00, df=1,10, p>0.10; F=0.47, df=1,10, p>0.10; respectively). Neither diet pattern (F=1.44, df=1,10, p>0.10) nor species (F=1.09, df=1,10, p>0.10) affected the proportion of snail consumed. Based on proportion plant and <u>Dreissena</u> in their diets, 'macrophyte-consumer' and 'mussel-consumer' classifications identified waterfowl that had significant diet differences.

There were no significant differences in the proportions of plant, snail, or <u>Dreissena</u> in any Fighting Island 'plant-consumer' species of waterfowl (ANOVA, df=5,18, p>0.05). These waterfowl included mallard, redhead, canvasback, bufflehead, as well as lesser and greater scaup 'macrophyte-consumers'.

Results of a 2-way ANOVA on proportion <u>Dreissena</u> in diet of lesser and greater scaup 'mussel-consumers' from Fighting Island (85 and 67%) and Lake Erie (100 and 97%) revealed both site (F=113.30, df=1,15, p<0.01) and species (F=24.44, df=1,15, p<0.01) differences, though the site\*species interaction was insignificant (F=0.80, df=1,15, p>0.10). Diets of both lesser and greater scaup from Lake Erie contained a higher proportion of zebra mussels than Fighting Island individuals (Figure 5, 6). However, Fighting Island lesser scaup ingested insignificantly different proportions of zebra mussels than greater scaup (Student's t-test, t=2.45, p=0.0701), as well Lake Erie lesser and greater scaup utilized similar amounts of <u>Dreissena</u> (t=1.43, p>0.10). The proportion snail utilized by Fighting Island and Lake Erie scaup did not differ by site (2-way ANOVA, F=1.15, df=1,15, p>0.10) or by a site\*species interaction (F=0.29, df=1,15, p>0.10), though species differences were evident (F=13.21, df=1,15, p<0.01). However, lesser

and greater scaup consumed similar amounts of snail at both Lake Erie (Student's t-test, t=1.44, p>0.10) and Fighting Island (t=1.52, p>0.10) sites. Mussel-consumer Fighting Island lesser and greater scaup consumed significantly higher proportions (15 and 24%) of macrophytes than Lake Erie (0%) individuals (2-way ANOVA, F=97.22, df=1,15, p<0.01), Though no significant species (F=1.70, df=1,15, p>0.10) or site\*species effects (F=1.70, df=1,15, p>0.10) were evident (Figure 5, 6).

A series of Student's t-tests were run on transformed diet proportions of plant, snail, <u>Dreissena</u>, and in some cases, amphipod, for two categories of waterfowl. One group was analyzed for both diet and contaminants, while the other was analyzed for diet only. Of all possible tests (see groups in Table 1) only a few revealed significant differences in consumption of specific diet items. Fighting Island bufflehead that were analyzed for contaminants utilized significantly more snail than non analyzed birds (t=2.71, p<0.05). Lake Erie bufflehead analyzed for contaminants consumed significantly more <u>Dreissena</u> (t=3.17, p<0.05) and less amphipod (t=3.55, p<0.01) than Lake Erie individuals not analyzed for contaminants. All other combinations resulted in insignificant differences with respect to diet content (p>0.05). Thus, in general, waterfowl used for GC analysis were representative of all individuals collected.

Waterfowl from Lake Erie consumed significantly different (Kolmogorov-Smirnov,  $\alpha$ =0.016) size classes of <u>Dreissena</u> (Figure 7). Bufflehead, the smallest diving duck studied, consumed the smallest mussels, while greater scaup consumed the largest mussels. Lesser scaup consumed intermediate size <u>Dreissena</u>.

#### Contaminant Concentrations and Profiles

Lipid normalized liver concentrations were regressed on wing tissue concentrations for 39 compounds obtained from 11 ducks. For all compounds the correlations were high ( $R^2$ >0.65) except for PCBs # 52, 49, 60, 70, 97, and 77 which had insignificant regressions of (linear regression,  $R^2 \le 0.14$ , p>0.10) (Table 4). Dieldrin, mirex and PCB # 101 had correlation coefficients between 0.55 and 0.65. Most compounds had concentrations close to or greater than a 1:1 ratio in liver to wing, except PCBs # 52, 49, 60, and 70 which were  $\le 0.55$ , and PCB # 97 which had a negative relationship.

Concentrations of most contaminants were strongly related to diet and location (Figures 8, 9, 10, 11). For example, no contaminant averaged more than 50 µg kg<sup>-1</sup> lipid in any Fighting Island duck that avoided <u>Dreissena</u> (Figures 8, 9, 10, 11), except for dieldrin and PCB # 138 in mallard, p,p'-DDE and PCB # 153 in canvasback, and dieldrin, p,p'-DDE, OCS, PCBs # 118, 138, and 153 in bufflehead (Appendix A). By comparison, however, conspecifics (bufflehead, greater and lesser scaup) that consumed Lake Erie <u>Dreissena</u> exceeded 150  $\mu$ g kg<sup>-1</sup> lipid for an array of compounds including dieldrin, p,p'-DDE, OCS and PCBs # 149, 118, 138, 153, 180, 201 and 206 (Figures 9, 10, 11). Diet differences both among and within sites influenced contaminant profiles and concentrations (Figures 8, 9, 10, 11). For example, ducks that consumed macrophytes and snails tended to have relatively high concentrations of low Kow compounds, while higher Kow compounds were typically present in higher concentrations in ducks that utilized mussels (Figures 9, 10, 11). PCB coplanar congeners # 77, 126, 169, and 189 were present in very low concentrations in all waterfowl (see Appendix A for congener # 77). Concentrations of total PCB as well as individual congeners were highest in Lake Erie greater scaup and other 'mussel consumer' groups of waterfowl (Appendix A).

Fighting Island wateriowl that consumed mussels had consistently higher concentrations of contaminants than conspecifics that had little or no <u>Dreissena</u> in their diet. As examples, relative to individuals with largely macrophyte diets, average concentrations were always higher for QCB (1.3 to 1.4x), p,p'-DDE (10.4 to 16.1x), OCS (1.9 to 38.5x), PCBs # 28 (1.1 to 0.55x), 105 (2.5 to 9.2x), 153 (4.5 to 12.9x), 180 (4.5 to 23.3x), 194 (4.1 to 18.2x) and 206 (5.6 to 18.1x) in lesser and greater scaup respectively that consumed mussels (Table 5). Almost without exception, differences were even more profound between Lake Erie scaup and Fighting Island 'macrophyte-consumer' scaup (Table 5).

Diet and species effects were explored by testing each of six compounds (QCB, PCBs # 28, 105, 153, 194, 206) as log K<sub>OW</sub> representatives in lesser and greater scaup from Fighting Island (Table 6). No significant species (2-way ANOVA, p>0.10) or species\*diet interaction effects (p>0.10) were observed for any of these compounds. However, 'mussel-consumers' had slightly but insignificantly higher concentrations of PCBs # 105 and 153 (p=0.0631 and p=0.0508; respectively) than ducks from the same site that consumed little <u>Dreissena</u>. Significantly higher concentrations of PCBs # 194 and 206 (p<0.05) were detected in 'mussel-consumers'. Thus, only moderate to high K<sub>OW</sub> compounds accumulated to a greater extent in scaup that consumed mussels (Figures 10, 11).

Contaminant levels in Lake Erie 'mussel-consumer' lesser and greater scaup were generally two to fourteen times higher than levels in 'mussel-consumer' conspecifics from Fighting Island (Table 5). Contaminant concentrations for 'mussel-consumer' scaup did not vary by species (p>0.10) or by species\*site interactions (p>0.10) for any of the six compounds selected (QCB, PCBs # 28, 105, 153, 194, 206) (2-way ANOVAs). For each of these compounds except QCB, Lake Erie scaup had significantly higher concentrations than individuals from Fighting Island (p<0.05) (Table 7; Figures 10,11).

Among bufflehead, Lake Erie ducks had two to ten times higher concentrations of most compounds relative to individuals from Fighting Island (Table 5). Similarly, 'mussel-consumer' Lake Erie bufflehead had significantly higher concentrations of PCBs # 153, 194 and 206 than Fighting Island conspecifics that consumed mainly macrophytes (Student's t-test,  $\alpha$ =0.0085) (Figure 9); slight but insignificant (p=0.0104) differences in concentrations of PCB # 105 were found in the two consumer groups, while concentration differences among groups for low K<sub>OW</sub> compounds (QCB, PCB # 28) were not evident (p>0.10). Finally, mallard from different sites (Fighting Island and Big Creek) did not vary significantly with respect to concentrations of any of the six compounds tested (Student's t-test,  $\alpha$ =0.0085).

Fighting Island zebra mussel contaminant levels were generally higher relative to Lake Erie <u>Dreissena</u>. However, concentration differences between sites were insignificant (Student's t-test,  $\alpha$ =0.0085) for the six compounds tested (QCB, PCBs # 28, 105, 153, 194, 206). Contaminant patterns for the two mussel samples were similar and were much elevated compared to macrophytes from Fighting Island (Figure 12).

Biomagnification factors for Lake Erie lesser and greater scaup varied by chemical K<sub>OW</sub> (ANCOVA, F=73.39, df=1,63, p<0.01) and by species (F=6.28, df= 1,63, p<0.05), though not by a species\*K<sub>OW</sub> interaction (F=0.12, df=1,62, p>0.10). BMFs tended to be higher for greater scaup compared to lesser scaup, and varied according to contaminant log K<sub>OW</sub> (Figure 13). Most BMFs were less than 4, though values for p,p'-DDE, OCS, mirex and PCBs # 195 and 206 were quite high (≥4). The highest BMF (21.7) was observed in greater scaup for the most hydrophobic substance (PCB # 206) studied.

#### Principal Component

Principal component analysis was conducted on contaminant data for 52 ducks, representing all six species, using four low-, mid- and high-K<sub>OW</sub> compounds. Principal component 1 (PC 1) accounted for 45% of the original data variability, and was determined primarily by high K<sub>OW</sub> compounds (PCBs # 206, 153, 194, 180, 105; Table 8). Principal component 2 (PC 2) accounted for an additional 18% of the variability and was determined by low-K<sub>OW</sub> compound QCB. Principal component 3 (PC 3) was determined by the low-K<sub>OW</sub> compound PCB # 28 and accounted for 10% of original data variability (Table 8).

Waterfowl that consumed mainly <u>Dreissena</u> separated on PC 1 and PC 2 from those that avoided <u>Dreissena</u>. Mussel 'consumer' and 'macrophyte-consumer' ducks had high and low PC 1 scores, respectively, with Fighting Island ducks with a <u>Dreissena</u> diet (though supplemented with macrophyte) located closer to other 'mussel-consumer' groups (Figure 14). Canvasbacks had the highest PC 1 score of any species that avoided <u>Dreissena</u>, due largely to relatively high concentrations of PCBs # 105, 153, 180, 194, and 206 in two of the ducks studied (see Appendix A). Differences in PC 2 scores depended primarily on relatively small, absolute differences in concentrations of QCB (<10 µg kg<sup>-1</sup> lipid) and HCB (<30 µg kg<sup>-1</sup> lipid).

Two-way ANOVAs were conducted to determine whether PC 1 and 2 scores varied by species or by location for 'mussel-consumer' scaup. No significant site (F=0.71, df=1,15, p>0.10), species (F=0.27, df=1,15, p>0.10) or site\*species (F=0.98, df=1,15, p>0.10) effects were detected with respect to PC 1 scores for scaup from different locations. Similarly, no significant species (F=0.58, df=1,15, p>0.10) or species\*site (F=0.87, df=1,15, p>0.10) effects were observed with respect to PC 2 scores, though there was a slight but insignificant (F=3.95, df=1,15, p=0.0654) difference in PC 2 scores by site for scaup; PC 2 scores

tended to be slightly lower for Lake Erie scaup relative to Fighting Island individuals (Figure 14).

Fighting Island greater and lesser scaup PC 1 scores differed significantly by diet (F=6.92, df=1,10, p<0.05) but not by species (F=0.53, df=1,10, p>0.10) or by a diet\*species interaction (F=0.14, df=1,10, p>0.10). Indeed, scores for Fighting Island scaup that consumed and avoided mussels were located near opposite ends of the PC 1 axis. While 'macrophyte-consumers' differed from conspecifics that consumed mussels on this axis, their scores were very similar to those of other waterfowl taxa that avoided <u>Dreissena</u> (Figure 14). PC 2 scores of Fighting Island scaup did not vary by species (2-way ANOVA, F=1.38, df=1,10, p>0.10), diet (F=1.04, df=1,10, p>0.10) or by an interaction (F=0.05, df=1,10, p>0.10) of these factors.

PC 1 score for Lake Erie 'mussel-consumer' bufflehead was significantly (Student's t-test, t=5.07, df=7, p<0.05) higher than that of Fighting Island individuals that ate little <u>Dreissena</u>, though no difference was detected with respect to PC 2 scores (t=1.89, df=7, p>0.10). Although these findings are consistent with results for scaup (Figure 14), they are confounded by site.

Big Creek mallard and Fighting Island waterfowl that avoided <u>Dreissena</u> (i.e. mallard, canvasback, redhead, bufflehead, and some greater and lesser scaup) did not differ with respect to PC 1 scores (1-way ANOVA, F=0.64, df=6,21, p>0.10), though PC 2 differences were significant (F=3.35, df=6,21, p<0.05). Bufflehead had slightly but insignificantly (Scheffé's test, p=0.0785) higher PC 2 scores than those of Big Creek mallard.

### <u>Stable Isotope</u>

Stable isotope results revealed that samples clustered into three groups: macrophytes and snails from Fighting Island, <u>Dreissena</u> and 'macrophyte-

consumer' ducks from Fighting Island, and a final cluster of Lake Erie 'musselconsumer' and Fighting Island 'plant-consumer' ducks (Figure 15). MANOVA on scaup (greater and lesser) indicated no significant difference by species for either  $\delta^{13}$ C (F=0.40, df=1,8, p>0.10) or  $\delta^{15}$ N (F=0.01, df=1,8, p>0.10). Scaup <sup>13</sup>C signatures do not differ by diet (F=0.00, di=1,8, p>0.10), unlike <sup>15</sup>N signatures which were significantly higher in 'mussel-consumer' ducks (F=9.79, df=1.8, p<0.05) than in 'macrophyte-consumer' ducks, with multivariate Hotelling-Lawley Trace being significant (F=4.92, df=2,7, p<0.05). No significant species\*diet interaction terms were observed for either carbon (MANOVA, F=3.19, df=1,8, p>0.10) or nitrogen (F=0.09, df=1,8, p>0.10) isotope values. Two-way ANOVA on all waterfowl indicated that carbon signatures differed neither by duck species (F=0.62, df=5,17, p>0.10) nor by diet (F=0.01, df=1,17, p>0.10). However, nitrogen signatures differed significantly by species (F=4.24, df=5,17, p<0.05) and diet (F=11.21, df=1,17, p<0.01). Nitrogen signatures in 'mussel-consumer' ducks were higher than those of 'plant-consumer' waterfowl. All Fighting Island 'macrophyte-consumer' ducks also differed significantly with respect to  $\delta^{13}C$ values relative to macrophyte, their putative food source (Dunnett's test, df=16, p<0.01). Nitrogen signatures were also significantly different in Fighting Island 'macrophyte-consumer' waterfowl and macrophyte food sources (1-way ANOVA, F=8.03, df=6,16, p<0.01); significantly higher levels of  $\delta^{15}$ N were found in bufflehead, canvasback, and redhead as compared to macrophyte (Dunnett's test, df=16, p<0.01). In the Lake Erie food chain, 'mussel-consumer' scaup did not differ from Middle Sister <u>Dreissena</u> with respect to either  $\delta^{13}C$  (1-way ANOVA, F=1.43, df=2,5, p>0.10) or  $\delta^{15}$ N (F=1.81, df=2,5, p>0.10) signatures. However, greater scaup nitrogen signatures were significantly higher than those of Dreissena (Student's t-test, t=9.06, p<0.01). Carbon signatures of greater scaup and <u>Dreissena</u> did not differ significantly (t=0.71, p>0.10). Similarly,  $\delta^{13}$ C and

 $\delta^{15}$ N signatures were similar in lesser scaup and <u>Dreissena</u> (t=0.93, p>0.10; t=1.40, p>0.10; respectively).

.

### Discussion

Detroit River sediments are extensively polluted with organochlorine compounds (Furlong et al. 1988), and river inputs serve as the primary source (73%) of organochlorine compounds into western Lake Erie (Kauss and Hamdy 1985; Carter and Hites 1992). Koslowski et al. (1994) observed significant accumulations of a wide array of organochlorine compounds in the Lake Erie food web, and argued that trophic interactions may play an important role in contaminant exposure. Results from this study indicate that recent diet is a good predictor of relative contaminant concentration in lower Great Lakes' waterfowl. These patterns hold both between (Lake Erie vs. Fighting Island) and within (Fighting Island) sites. For example, ducks that consumed Dreissena tended to have elevated concentrations of most contaminants relative to conspecifics that had little or no <u>Dreissena</u> in the diet (Figures 10, 11). Small sample sizes used to determine contaminant concentration differences in conspecifics revealed significant differences in some mid- and all high-Kow compounds, however, larger sample sizes may have determined significant differences in all mid-Kow representatives. At present it is not possible to determine whether these patterns are owing to disproportionate effects on contaminant concentrations of recent feeding, or whether fidelities of waterfowl to particular food types is pronounced.

# Waterfowl Predation of Mussels

Many studies have explored the distribution of waterfowl with respect to habitat, food resources, competition, and disturbance (McCullough 1981; Prince et al. 1992; Einarsson and Magnusdottir 1993; Haramis et al. 1993; Nummi and Poysa 1993; Fox et al. 1994; Gardarsson and Einarsson 1994; Michot et al. 1994; Winfield and Winfield 1994). A number of workers have implicated <u>Dreissena</u>

prev as a primary factor influencing waterfowl distribution (Stanczykowska et al. 1990; Wormington and Leach 1992; Mitchell and Carlson 1993; Hamilton et al. 1994; Suter 1994). Valuable insights into waterfowl-Dreissena interactions have emerged from studies of migrating waterfowl. Stempniewicz (1974) calculated that coot were responsible for a reduction of 32.5% Dreissena biomass, and 70% of yearly mussel production in Lake Goplo, Poland. Stanczykowska et al. (1990) estimated that waterfowl could remove up to 20.2% of the annual production of Dreissena in areas of Lake Zegrzynskie, Poland, owing to intense foraging by high densities of migrant diving ducks. The location of congregating waterfowl coincided with areas of mass occurrence of Dreissena, suggesting active selection of foraging sites by these birds. In a field study, Draulans (1982) described significant increases in predation rate by tufted ducks following increases in Dreissena density; in addition, predation caused a significant change in size composition of the mussel population through selective harvest of 1-1.75 cm mussels. Also, mussel densities at 2 - 3 m depth, which were easily accessible to waterfowl, decreased significantly more than those at 4 - 6 m depth (Draulans 1982). In a region of the upper Rhine river that supported high <u>Dreissena</u> biomass (9.9 - 12 kg m<sup>-2</sup> fresh biomass) and densities, tufted ducks and coots consumed over 90% of the standing biomass during their winter stay (Suter 1982; Cleven and Frenzel 1993). Each autumn, mussel biomass was fully restored and the population consisted almost entirely of 1-year olds that apparently emigrated from a refuge population that existed beyond the diving capabilities of the waterfowl. Indeed diving waterfowl are considered the most voracious predators of Dreissena; however, control of Dreissena populations by waterfowl is temporal at best, as Dreissena's reproductive potential, migration ability, and growth rates allow re-establishment of mussel populations.

Intense predation by waterfowl on Dreissena parallels results from marine systems. For example, Faldborg (1994) described a Danish Wadden Sea population of blue mussels (Mytilus edulis) that consisted of a single year class characterized by failed recruitment over 6 years. The population declined from 8,000 individuals m<sup>-2</sup> to 1,500 individuals m<sup>-2</sup>. Waterbirds, mainly common eiders, oystercatchers and herring gulls, were estimated to remove 64% of the blue mussel biomass production in the third year. Despite intensive predation by waterbirds, steady growth rates of the mussel cohort resulted in an increase in total biomass sufficient to support the eider population. Plagued by years of failed recruitment and intensive fishing, the mussel beds on tidal flats of the Dutch Wadden Sea were virtually eliminated (Beukema 1993). Predation of Dreissena by waterfowl depleted stocks on the river Rhine and the western Wadden Sea to the point that waterfowl experienced food shortages (Suter and Van Eerden 1992). In combination with an unusual cold spell in 1986, starvation resulted in the deaths of an estimated 2,700 - 6,200 river Rhine and 14,000 Wadden Sea diving ducks (mainly scaup, tufted duck, goldeneye, pochard, and eider) (Suter and Van Eerden 1992).

Predation on <u>Dreissena</u> by North American waterfowl has also been documented (Wormington and Leach 1992; Mitchell and Carlson 1993; Hamilton et al. 1994; R. Knapton, pers. comm.; C. Custer, pers. comm.). Wormington and Leach (1992) recorded 13,500 lesser scaup (90 times historical counts) in maximum one-day counts of waterfowl off the Point Pelee shore. Field observations of waterfowl predation were confirmed by analysis of digestive tracts (Wormington and Leach 1992). Also evident was an increase in stopover duration as birds lingered in the area longer. The availability of <u>Dreissena</u> as a food source has altered the migratory behaviour and distribution of some diving ducks, mainly lesser and greater scaup (Wormington and Leach 1992). In Lake

Michigan, Mitchell and Carlson (1993) found that lesser scaup consumed zebra mussels exclusively. The zebra mussels had only settled on the water intake structures of Cook nuclear plant the preceding year, yet migrating waterfowl found this new food source almost immediately. Twenty-one lesser scaup obtained from Cook Nuclear Plant ingested much smaller size mussels of 4.1 mm (Mitchell and Carlson 1993) compared to 11.2 mm mussels consumed by lesser scaup from this study. In the fall of 1991, Hamilton et al. (1994) determined that waterfowl staging off of Point Pelee, Ontario, consumed 57% of Dreissena biomass in near shore waters. Predation was size selective, as ducks chose individuals between 11 and 21 mm. Size selective predation altered the size structure of the mussel population in that area. However, as very few birds remained after mid-winter, mussel populations regained biomass and abundance by spring 1992. Because this region of the lake is very shallow and should therefore experience maximal impact, duck predation probably exerts only ephemeral regulatory effects on the Lake Erie Dreissena population. Similar effects would be expected on mussel beds located in Lake St. Clair, a proximal shallow lake that is intensively utilized by migrating diving ducks.

# Contaminant Concentrations

Uptake and assimilation of polychlorinated biphenyls is considered to occur very rapidly in waterfowl (Weseloh et al. 1994). Gebauer and Weseloh (1993) reported accumulation of PCBs in domestic mallard 5,300 times higher than initial levels within ten days of natural exposure to contaminants. Mallard exposed to dieldrin achieved steady state concentrations in muscle, liver, skin, and fat within 7 - 8 days and depuration was estimated to be at least 3 weeks (Nebeker et al. 1994). Thus migrating waterfowl are susceptible to short term contaminant exposure and body burdens should reflect prior exposure.

Significant positive regressions between lipid normalized concentrations in liver and wing of 11 ducks were observed for all but 6 of 39 compounds studied. Metabolism and/or low environmental concentrations may have influenced the very low concentrations detected in liver and wing for these compounds. The strong influence of relatively high wing or liver concentrations in one or two samples disrupted potential correlations for PCBs # 49, 52, 60, 70, 77, and 97. Total lipid-adjusted PCB levels in the 11 duck subsample were on average 1.23 times higher (range 1.06 - 1.95) in liver than in muscle. On a wet weight basis, values were an average of 2.2 times higher (range 1.04 - 7.35) in liver than in wing muscle.

The relationship between contaminants in scaup was diet dependent as Fighting Island 'plant-consumers' were the least contaminated, intermediate levels were encountered in Fighting Island 'mussel-consumers', and Lake Erie 'musselconsumers' were most contaminated. The relationship is even more complex, as higher log K<sub>OW</sub> compounds were more prevalent in 'mussel-consumers' and low K<sub>OW</sub> compounds more prevalent in 'plant-consumers'. For example, the proportion of total PCBs contributed by a single congener increases for high log K<sub>OW</sub> compounds in each successive trophic 'tier' (Figure 16). The tendency of selective compounds to bioaccumulate through food chains has been documented in aquatic systems involving zooplankton, fish, herring gulls, and sea birds (Connolly and Pederson 1988; Oliver and Niimi 1988; Braune and Norstrorn 1989; Boumphrey et al. 1993; MacDonald et al. 1993; Koslowski et al. 1994; Russell et al. 1995).

When contrasted against Fighting Island 'plant-consumers', co-occurring 'mussel-consumers' had similar, slight but insignificantly higher, and significantly higher concentrations of the pairs of low-, mid-, and high- K<sub>OW</sub> representatives (Figures 10, 11). If sample sizes were larger the differences between mid-K<sub>OW</sub>

representatives may have been significant. Select congeners such as PCBs # 180, 194, and 206 were 23.3, 18.2, and 18.1 times higher in 'Dreissenaconsumer' scaup. A similar pattern of chemical fate was observed between 'mussel-consumer' scaup from Lake Erie versus those from Fighting Island, where 5 out of 6 log Kow representatives were significantly higher in Lake Erie waterfowl (Figures 10, 11). Although absolute levels of contaminants are highest in the lake group, PCBs # 180, 194, and 206 were only 3.4, 3.9, and 14.0 times higher than in Fighting Island conspecifics. Considering Fighting Island Dreissena were somewhat more contaminated than Lake Erie mussels, it is surprising that Lake Erie scaup were more contaminated. This pattern may be due to diet differences, as Lake Erie ducks consumed significantly more mussels (~100%) whereas Fighting Island individuals periodically consumed plants which limited mussel intake (~75%). The fidelity to which waterfowl maintain these diets was not studied; however, on occasion Fighting Island scaup were observed to rest and feed in areas of lush marsh plants and macrophytes (pers. obs.). Unfortunately, Fighting Island 'mussel-consumer scaup' were not analyzed for  $\delta^{13}C$  and  $\delta^{15}N$ isotopes. Thus, it was not possible to ascertain whether these scaup had fed on a mixed Dreissena-macrophyte diet in the recent past. By contrast, immense flocks of Lake Erie diving ducks have been observed feeding for months in areas where the benthos is dominated by Dreissena (Wormington and Leach 1992; Hamilton et al. 1994).

A similar condition exists between bufflehead, where the Lake Erie 'musselconsumer' group were significantly more contaminated than the Fighting Island group for 3 of the 6 higher-K<sub>OW</sub> organochlorine representatives (Figure 9). Organochlorine contaminant concentrations in all plant-consumer waterfowl in this study were similarly quite low and in agreement with or slightly higher than levels determined in two plant-consumer hatching-year lesser scaup collected from

Blackstrap Lake, Saskatchewan (unpubl. data). Among plant-consumer waterfowl, bufflehead were the most contaminated. This was expected since Fighting Island bufflehead consumed 20% animal matter and had elevated  $\delta^{15}$ N values relative to ducks that ate only macrophytes. Lake Erie bufflehead consumed smaller <u>Dreissena</u> than lake scaup yet bufflehead were more contaminated than lesser scaup. Since bufflehead were preying on smaller, less contaminated, <u>Dreissena</u> (Morrison unpubl. data) they would be expected to be less contaminated than lesser scaup. It is possible that bufflehead may have received exposure to higher levels of contaminants through amphipod which comprised 26% of bufflehead diet.

Evidence of metabolism of compounds was not discernible. Patterns of compounds in plant-consumer scaup (Figure 10, 11) were similarly low in macrophytes (Figure 12). Lake Erie scaup (Figure 10, 11) contaminant patterns resembled those of Lake Erie <u>Dreissena</u> (Figure 12); major chemical peaks were consistent. If a compound was apparent in the prey species yet absent or only detectable at low concentrations in the predator then efficient metabolism of that compound could be invoked.

This study revealed very low (<10  $\mu$ g kg<sup>-1</sup>) concentrations of coplanar PCBs (# 77, 189, 126, 169) in all ducks, though concentrations of the former two were highest in mussel consumers from Lake Erie. By contrast, Koslc wski et al. (1994) reported concentrations of PCB # 77 in carp, gizzard shad, silver bass, smallmouth bass and herring gull eggs up to forty times the maximum values recorded here.

Biomagnification factors for p,p'-DDE, octachlorostyrene, mirex, and PCBs #195 and 206 ranged between 4.0 and 21.7 in greater scaup. Octachlorostyrene and mirex may be assimilated from different sites i.e. OCS is prevalent in the upstream St. Clair River and Lake St. Clair (Kovats and Ciborowski 1993), while

mirex is more or less isolated to downstream Lake Ontario (Kaiser 1978). Mobile waterfowl could be exposed to these contaminants, though the zebra mussels studied here would not be, leading to high BMFs. PCBs # 195 and 206 have such high Kow values that once incorporated these chemicals are retained to a higher degree than low Kow compounds (Wolff and Schecter 1991; Brieger and Hunter 1993). As well, high Kow compounds are very hydrophobic and are less likely to be associated with the water column and lipid-poor plankton. Nevertheless, exposure through suspended sediment and trace levels in algae and water can result in uptake of these compounds in mussels (Brieger and Hunter 1993; Fisher et al. 1993). However, consumption of mussels leads to exposure to contaminants recently acquired by the mussels. Zebra mussels are not exposed to these congeners to the same extent or duration that greater scaup are exposed, possibly explaining the high BMFs observed. Most biomagnification factors increased from 1 - 4 as Kow increased, which is consistent with findings of Russell et al. (1995). However, absolute BMFs for PCBs # 52, 87, 138, and 180 in greater scaup were respectively only 10, 37, 82, and 54% relative to BMF values reported in white bass of western Lake Erie (Russell et al. 1995). Russell et al. (1995) demonstrated that lipid levels of white bass intestinal contents (emerald shiners) decreased significantly as prey items were digested. Subsequently the fugacity capacity of the prey items decreased and chemical concentration in these digested intestinal contents increased. This resulted in a fugacity gradient between the intestinal contents and the white bass that was adequate to drive biomagnification of high Kow compounds (PCBs # 87, 138, and 180). Russell et al. (1995) concluded that chemical concentration differences between emerald shiner and digested emerald shiner suggest a fugacity model of chemical accumulation not exclusive of a lipid co-assimilation model. Tufted ducks have fast metabolism, and therefore they ingest and excrete relatively large quantities

(35%) of organic material (Gere and Andrikovics). Perhaps waterfowl are less efficient in lipid assimilation than fish explaining the lower biomagnification factor values of waterfowl relative to white bass.

Rasmussen et al. (1990) investigated values of biomagnification factors in lake trout from a series of lakes with progressively longer food chains. Trout from lakes with longer food chains were associated with higher absolute levels of total PCB. Rasmussen et al. (1990) reported total PCB biomagnification factors of 3.5 per trophic level. Congener specific BMFs were not available for comparison.

Greater scaup that consumed mussels tended to have higher concentrations (and BMFs) of most contaminants than lesser scaup from the same location that also fed on <u>Dreissena</u>. It is not clear what factors may account for this pattern, though greater scaup ingested significantly larger mussels than lesser scaup (Figure 7). Because larger mussels have higher lipid-normalized contaminant concentrations (Morrison unpubl. data), greater scaup may be exposed to higher levels of contaminants than lesser scaup consuming essentially the same resource. The divergence of contaminant profiles of waterfowl at one location feeding on one food type indicates that contaminant exposure may vary both as a function of trophic position and by feeding strategy (Connolly and Pederson 1988; Evans et al. 1991; Koslowski et al. 1994). In particular, feeding strategy could complicate attempts to model contaminant exposure if individuals select seemingly similar food items that, in fact, differ considerably in contaminant levels.

Although lesser and greater scaup in this study are migratory it is likely that contaminants were assimilated in the study area, rather than from other locations visited throughout their flyway (Figure 17). Field and laboratory studies show that waterfowl can assimilate organic contaminants within 10 days (Gebauer and Weseloh 1993; Weseloh et al. 1994) and may depurate them in just over three weeks (Nebeker et al. 1994). Limited data show that migrating juvenile scaup

collected before they reach the Great Lakes possess very low contaminant concentrations (unpubl. data). Lake Erie hatching year scaup that consumed <u>Dreissena</u> were contaminated with patterns consistent of <u>Dreissena</u> and consistent to concentrations in adult scaup. Because hatching year scaup had not yet frequented the East Coast their contaminant burdens cannot be attributed to accumulation at these southern localities.

Although contaminant levels were elevated in scaup that consumed Dreissena, concentrations in these individuals are much lower than those reported for these species from the Detroit River (Table 9). For example, Smith et al. (1985) reported p,p'-DDE whole carcass (field dressed) wet weight concentrations between 8 and 13 times higher than the maximum values observed in this survey for lesser and greater scaup. The disparity between contaminant levels observed here and in the Smith et al. (1985) study may be owing to sample preparation techniques and resulting differences in lipid levels of analyzed tissues. For instance, Smith et al. (1985) used field dressed lesser and greater scaup, the mixed tissue of which contained mean lipid levels of 17.8 and 16.3%, respectively. These values are 3.6 and 2.9 times higher than liver lipid levels from Lake Erie scaup in this study. It has been demonstrated that PCB and DDE levels can be 25 - 40 and 20 - 90 times higher, respectively, in fat tissue as compared to muscle in waterfowl (Table 9) (Kim et al. 1984; Foley 1992; Swift et al. 1993). Smith et al. (1985) also reported that total PCB concentration increased with decreasing lipid concentration in lesser and greater scaup and goldeneye collected in the Detroit River. This suggested differential PCB mobility, since more persistent (higher Kow compounds) were retained and lower Kow compounds were lost as lipid reserves were utilized over the course of winter. No such pattern was apparent in this study, though lipid levels in liver varied much less (3.3 -5.7%) than in whole bird carcasses of Smith et al.'s study (~6 - 26%).

Levels of contaminants (HCB, trans-nonachlor, p,p'-DDE, oxychlordane, dieldrin, and total PCBs) in waterfowl from this study are compared with values from other studies in Table 9. Because congener specific concentrations in waterfowl liver tissue are scarce in the literature, comparisons are based on total PCB concentrations. Excluding values obtained from whole carcass, fat tissue and those in mergansers, levels of all six contaminants in 'mussel-consumer' Middle Sister waterfowl are in agreement with results from other studies. Mergansers are piscivorous waterfowl and tend to have elevated levels of contaminants (Weseloh 1986). Contaminant levels in the Fighting Island 'plantconsumers' are among the lowest reported in any of the studies. The use of adipose tissue as a common currency in future studies would be recommended owing to high concentrations of contaminants that can be detected in this tissue.

Herring gulls nesting on Middle Sister Islands have total PCB concentrations at least 1 order of magnitude higher than Lake Erie scaup from this study (G. Fox, pers. comm.). Greater and lesser scaup wet weight DDE levels are also at least two orders of magnitude lower than values reported for eggs of double-crested cormorants, Caspian terns and Forster's tern from a variety of Great Lakes locations (Kubiak et al. 1989; Yamashita et al. 1993). These results are not surprising since species of fish-eating birds are considered to be at a higher trophic level than 'mussel-consumer' waterfowl.

### Principal Component

Principal component analysis was performed on liver contaminant data (12 organochlorine compounds) in six Great Lakes species of waterfowl. Principal component one was determined by high K<sub>OW</sub> compounds while components two and three were determined by low K<sub>OW</sub> compounds. All 'macrophyte-consuming' waterfowl had lower PC 1 scores relative to '<u>Dreissena</u>-consumer' ducks. Fighting

Island <u>Dreissena</u>-consumer scaup possessed significantly higher PC 1 scores than 'macrophyte-consumer' scaup while <u>Dreissena</u>-consumer scaup from Fighting Island and Lake Erie with similar diets had similar PC 1 scores. The influence of diet and not location on PC 1 scores was evident. Lake Erie Bufflehead 'mussel-consumer' individuals also had higher PC 1 scores in comparison with Fighting Island 'macrophyte-consumer' conspecifics.

## Stable Isotope

Although some of the stable isotope results are difficult to interpret, some patterns and associations were noted. As an assimilation time reference, laboratory-raised quail subjected to a dietary increase in  $\delta^{13}$ C experienced a comparable shift in muscle tissue in just over 25 days (Hobson and Clark 1992). Because fishermen and researchers have observed large flocks of diving waterfowl in the western basin of Lake Erie from October through December (Wormington and Leach 1992; Hamilton et al. 1994; G. Penner, pers. comm.), ducks should have had sufficient time for equilibration of different isotopes. Trophic level enrichment of <sup>15</sup>N is evident in Lake Erie scaup relative to <u>Dreissena</u> prey, averaging 2.6‰ in lesser scaup and 2.3‰ in greater scaup (Figure 15). Lesser scaup. As well, Lake Erie 'mussel-consumer' greater scaup were significantly enriched in <sup>15</sup>N (2.4‰) and <sup>13</sup>C (1.9‰) relative to 'plant-consumer' Fighting Island conspecifics (Figure 15). These examples indicate trophic enrichment of isotopes assimilated from <u>Dreissena</u>.

The basis of this food chain appears to be a  $\delta^{13}$ C source between -20 and -25‰, values consistent with phytoplankton and zooplankton (Peterson and Fry 1987; Junger and Planas 1993; Fry and Quinones 1994; Zohary et al. 1994); both of these trophic levels are accessible food sources for <u>Dreissena</u>. Plant-consumer

greater scaup, lesser scaup, and mallard aggregated with <u>Dreissena</u> in a lower trophic level isotope position ( $\delta^{15}N$  of 6 - 7‰) (Figure 15) and exhibit  $\delta^{13}C$  levels intermediate to terrestrial plants (-28‰; Peterson and Fry 1987) and macrophytes from this study (~-10‰). Because omnivores'  $\delta^{15}N$  signature are determined by their animal prey (R. Hesslein pers. comm.), Fighting Island bufflehead that consumed a diet of 20% snail and <u>Dreissena</u> should group with the higher  $\delta^{15}N$ trophic level 'mussel-consumer' Lake Erie scaup. Although Fighting Island redhead were not observed to consume animal matter in this study, their  $\delta^{15}N$ signatures suggests consumption of some animal diet items. Redheads have been documented to consume 13 to 42% animal matter (gastropods) and are omnivores (Michot and Nault 1993). As well, canvasback are known to consume marine mussels in Chesapeake Bay and are considered omnivores (Perry and Uhler 1988; Lovvorn 1989; Jorde et al. 1995). Both canvasback and redhead displayed higher  $\delta^{15}N$  signatures than expected relative to Fighting Island scaup.

Unfortunately, Fighting Island 'mussel-consumer' scaup and Lake Erie bufflehead were not analyzed for carbon and nitrogen isotopes. Subsequently, within site comparisons among scaup and bufflehead were not possible. Though unknown, their  $\delta^{13}$ C and  $\delta^{15}$ N isotope signatures might have been similar to Lake Erie scaup and Fighting Island bufflehead, owing to their substantial proportion of animal diet.

Trophic level differences between waterfowl 'mussel-consumers' and 'plantconsumers' have been defined by diet contents, organochlorine levels, and <sup>15</sup>N stable isotope signatures. Previous studies have employed stable isotopes to analyze trophic relationships and contaminant biomagnification for Great Lakes' systems (Rasmussen et al. 1990; Cabana and Rasmussen 1994; Keough 1994; Kidd et al. 1995). The research described here illustrates the value of stable isotopes to identify <u>Dreissena</u>-based food webs in the lower Great Lakes.

#### Reproductive Issues

Reproductive problems associated with organochlorine contaminants have been reported for a number of Great Lakes' waterbirds (see reviews, Fox 1993; Bosveld and Van den Berg 1994; Geisy et al. 1994). Concern has centered on the possibility that scaup which consume contaminated <u>Dreissena</u> may accumulate sufficient burdens of contaminants as to experience reproductive impairment. For example, European work demonstrated reduced clutch size, egg size, egg weight, and hatch success for captive tufted ducks fed contaminated Dreissena relative to a control group fed 'clean' mussels (de Kock and Bowmer 1993). Both sources of mussels occurred naturally in areas of different contaminant history and loadings. The control group of ducks successfully formed pairs, courted, built nests, laid eggs and incubated eggs resulting in 100% reproductive success. The 'contaminated' group built untidy nests and abandoned their nests after eggs were laid; all eggs would have perished in absence of parental incubation. As a consequence, seventeen abandoned eggs were artificially incubated, of which only 7 hatched. Embryo mortality accounted for 60% of the reproductive failure, which the authors attributed to high concentrations of maternally transferred PCBs found in the eggs (de Kock and Bowmer 1993). Respective mean liver concentrations of PCBs # 138, 153, and 180 in  $\mu$ g kg<sup>-1</sup> dry weight were 450, 520, and 175 in the contaminated group and 100, 100, and 45 in the control group (de Kock and Bowmer 1993). The highly contaminated group of waterfowl also had corresponding egg contaminant levels that were 2.1, 4.2, and 3.2 times higher than those found in liver. Lake Erie greater scaup, the most contaminated waterfowl in this study, had PCBs # 138, 153, and 180 mean liver concentrations of 124, 91, and 95 µg kg<sup>-1</sup> dry weight, respectively. These values correspond to 27.5, 17.5, and 54.3% of the levels found in the reproductively-impaired group from de Kock and Bowmer's (1993) study. Levels (µg kg-1 dry weight basis) were

higher in Lake Erie greater scaup than in the reproductively successful tufted duck controls for PCBs # 138 and 180 and similar for congener 153. Total PCBs (wet weight) in greater scaup were only 12.4% of those found in reproductively-impaired tufted duck from de Kock and Bowmer (1993).

Using toxicity equivalent factors from Safe (1992), 2,3,7,8-tetrachlorodibenzop-dioxin (TCDD) toxicity equivalents (TEQs) for Lake Erie greater scaup liver were calculated to be 20.6 ng TCDD kg<sup>-1</sup> wet weight and 460 ng TCDD kg<sup>-1</sup> lipid. Higher TEQs would be expected in eggs produced from these scaup. In a toxicity study, Murk et al. (1994) administered single intraperitoneal injections to eider ducklings using two different dosages of PCB # 77 and Clophen A50 (a PCB mixture). Respective, levels of TCDD-TEQs of 140 - 875 and 23 - 129 µg kg<sup>-1</sup> lipid were detected in internal eider abdominal fat, levels 50 - 1,900 times higher than greater scaup liver from this study. Ten days after exposure, significant correlations resulted between internal TEQs and parameters studied by Murk et al. (1994). Parameters with positive correlations with TEQs were relative liver weight, cytochrome P4501A activity (in PCB 77 and A50 groups), and plasma retinol levels and plasma retin/hepatic retinyl palmitate ratio (in PCB 77 group). Negative correlations occurred with body weight gain, beak length growth (in A50 group), and plasma thyroid-hormone and hepatic retinoid levels (in PCB 77 group). Murk et al. (1994) cautioned that eider ducks may be at risk to adverse health effects in highly contaminated areas due to their sensitivity to PCB toxicity. White and Seginak (1994) linked dioxins and furans to reproductive impairment in wood ducks. Wood duck eggs with a greater than 20 - 50 ng kg<sup>-1</sup> wet weight 2,3,7,8-TCDD TEQ were taken from nests which incurred significantly lower nest success (~30% clutch reduction), hatching success (~26% lower), and duckling production (~2 ducklings less) when compared to nests with cleaner eggs having TEQs <5 ng kg<sup>-1</sup> wet weight (White and Seginak 1994). One duckling from a failed nest

exhibited bill deformities and subcutaneous edema of the head and neck. Analysis of this embryo revealed whole body TEQ of 42 ng kg<sup>-1</sup> wet weight, a value approximately twice as high as those found in greater scaup livers.

Effects of PCBs and other compounds on waterfowl have been documented mainly through acute exposure studies involving contaminants. In mallard, dietary ingestion of 150 mg kg<sup>-1</sup> Arochlor 1242 was related to a decrease in eggshell thickness of 8.9% and PCB levels reached 100 mg kg<sup>-1</sup> wet weight in some of the same eggs (Haseltine and Prouty 1980). However, mallard fed a dietary dosage of 25 mg kg<sup>-1</sup> Arochlor 1254 demonstrated no reproductive impairment or decreased nest attentiveness (Custer and Heinz 1980). Heath et al. (1972) demonstrated related egg shell thinning, egg cracking, and reduction in hatching success in mallards fed 10 mg kg<sup>-1</sup> dietary DDE. Concentrations of DDE and PCBs were correlated with egg shell thinning in grebes (Forsyth et al. 1994). Nebeker et al. (1992) observed decreased activity, growth impairment and mortality in mallard ducklings exposed to as little as 16.4 mg kg<sup>-1</sup> dieldrin in feed; liver tissue concentrations reached ~28 mg kg<sup>-1</sup> wet weight within ten days. However, Nebeker et al. (1994), observed no effects of dieldrin on growth in mallard ducklings which accumulated 4.1 mg kg<sup>-1</sup> wet weight in liver. Greater scaup from lake Erie exhibited wet weight liver concentrations of 0.02 mg kg<sup>-1</sup> for both p,p'-DDE and dieldrin. Although effects of acute exposure to specific compounds on waterfowl are known to a limited degree, effects of long term chronic exposure are poorly understood.

Biological effects of organochlorine compounds are known to vary by orders of magnitude depending on the species being studied (Ikemoto et al. 1992; Peterson et al. 1993; Hoekstra et al. 1994). For this reason, species should be considered in interpreting bioassay results, just as tissue type and the mode of sample preparation (i.e. wet versus lipid) require consideration when evaluating

contaminant concentrations and effects. Nevertheless, Yamashita et al. (1993) reported PCB concentrations in double crested cormorant eggs from the Great Lakes that ranged from 3,600 to 7,300 µg kg<sup>-1</sup> (wet weight). These levels correspond to TCDD-TEQs of 334 - 1,280 ng kg<sup>-1</sup> (wet weight). Higher levels of total PCBs and coplanar PCBs were associated with 'live-deformed' cormorant embryos compared to normal embryos (Yamashita et al. 1993). Deformities included crossed bill and clubbed foot. In the same study, Caspian tern eggs from Saginaw Bay, Michigan, expressed PCB levels 2.6 and 3.4 times higher in infertile eggs and deformed-embryos than in normal eggs, respectively. Yamashita et al. (1993) concluded that TEQs was likely associated with the occurrence of livedeformed embryos in Great Lakes cormorant eggs and that non-ortho coplanar PCBs contributed most toward the TEQs. In the Netherlands, Dirksen et al. (1995) observed that cormorants in contaminated areas of Rhine and Meuse rivers had extremely reduced breeding success relative to other less-contaminated Dutch colonies. As well, significant correlations were found for egg DDE concentrations and eggshell thinning, and for egg PCB concentrations and hatching and breeding success (Dirksen et al. 1995). High reproductive impairment (75%) in Green Bay Forster's tern was associated with 11 fold higher TCDD TEQs (mean egg TEQ of 2,175 ng kg<sup>-1</sup> wet weight) relative to a reference colony (Kubiak et al. 1989). On a positive note, Harris et al. (1993) suggested that improved reproductive performance in Green Bay Forster's tern in 1988 was associated with lower egg PCB concentrations. The same colony had higher levels of reproductive failure and higher egg PCB levels in 1983. Although the levels of contaminants and organochlorine sensitivities may vary by species, an underlying association of higher levels of contaminants with increased reproductive impairment are evident in many avian species.

U.S. Fish and Wildlife midwinter counts have revealed declining scaup numbers in all flyways of the U.S. and Canada (summarized in Barclay and Zingo 1993). In North America, greater scaup fly through, among other areas, the Lake Erie region during migrations to and from Alaskan breeding grounds (Figure 17). Although birds staging on Lake Erie may avoid hunting pressure during the southerly fall migration, thereby decreasing adult and juvenile mortality (C. Custer pers. comm.), this benefit may be offset by contaminant-induced reproductive impairment. During 1993, greater scaup suffered an unusually high (37%) rate of reproductive failure in Alaska, where 25% of eggs were infertile and 12% were addled beyond classification (J. Barclay, pers. comm.). It is not known whether ducks that staged on Lake Erie and consumed Dreissena were among those that experienced reproductive problems in Alaska. However, lesser scaup chicks reared solely on a diet of zebra mussels from the Middle Sister Island area had depressed levels of vitamin A and a compromised immune system (C. Tessier, pers. comm.) and are summarized below. Results from the feeding study showed significant decreases in hexa- and copro-porphyrin in mussel-fed scaup compared to control animals fed contaminant free duck chow. As well, a significant decrease in retinol (active form of vitamin A) concentration occurred compared to controls, and phagocytic activity of immune cells was significantly reduced (27%). Liver masses of mussel-fed lesser scaup were significantly increased. However, no differences in EROD activity was observed between the 'mussel-fed' group and control individuals. These mussel-fed lesser scaup accumulated total PCBs of 1,600 µg kg<sup>-1</sup> lipid, in comparison Lake Erie greater scaup, lesser scaup, and bufflehead values were 4,464, 2,734 and 3,722  $\mu g$  kg  $^{-1}$ lipid, respectively. Clearly, however, additional work is warranted to identify whether greater scaup frequenting western Lake Erie experience reproductive impairment owing to consumption of contaminated Dreissena. Of concern is the

subsequent maternal transfer of organochlorine contaminants to eggs since developing embryos appear to be at greater risk than adults.

#### Summary

Different techniques were used to assess organochlorine contaminant profiles in Great Lakes' waterfowl. Waterfowl gut content analyses revealed diet varied among species, and between and within sites. Waterfowl from Fighting Island were classified into 'mussel-consumer' or 'macrophyte-consumer' groups based on 'snapshot' diet analysis. Lipid-adjusted liver concentrations of contaminants, mid- and high log Kow compounds, were marginally and significantly related to 'snapshot' diet; for example Fighting Island 'mussel-consumer' scaup typically had much higher concentrations of most contaminants relative to conspecific 'macrophyte-consumers' from that site. As well, 'mussel-consumer' bufflehead were more contaminated with the three higher log Kow representatives than individuals that consumed mainly macrophyte. Location effects were significant in 5 of 6 chemicals studied owing to higher concentrations of contaminants in 'Dreissena-consumer' Lake Erie scaup relative to Fighting Island individuals, possibly because lake scaup fed more intensively on mussels. Significant species differences occurred only between 'mussel-consumers' and 'macrophyteconsumers' species. Principal component analysis of log-transformed, lipidadjusted, liver contaminant concentrations separated waterfowl groups on components one and two based principally on diet differences.

Stable isotope analyses established that two separate trophic levels exist in the Lake Erie <u>Dreissena</u>-waterfowl component of the food web. Lake Erie scaup had elevated  $\delta^{15}$ N values relative to Lake Erie <u>Dreissena</u> and Fighting Island 'macrophyte-consumer' scaup. These differences approximated those observed between trophic levels in other aquatic ecosystems.

Toxic equivalents (TEQs) for Lake Erie greater scaup liver were calculated to be 20.6 ng TCDD kg<sup>-1</sup> wet weight and 460 ng TCDD kg<sup>-1</sup> lipid, which are one half

or less than the levels associated with reproductive impairment in wood duck. The effects of chronic exposure to levels of dieldrin, p,p'-DDE, and PCBs found in waterfowl in this study are not fully known except for diminished vitamin A and phagocytic immune responses. Greater scaup had the highest concentration of most contaminants in this study, and experienced reproductive failure during 1993 at Alaskan nesting grounds. However, it has not been established whether individuals that suffered reproductive failure had previously exploited contaminated <u>Dreissena</u> in the Great Lakes region.

This study illustrates that <u>Dreissena</u> has become fully integrated in lower Great Lakes food webs, and is responsible for alteration of contaminant pathways through modification of predator-prey relationships.

### References

- Barclay, J.S. and J.M. Zingo. 1993. Winter scaup populations in Connecticut coastal waters. Connecticut Warbler 13:136-150.
- Bartish, T. 1987. A review of exchange processes among the three basins of Lake Erie. J. Great Lakes Res. 13:607-618.
- Beukema, J.J. 1993. Increased mortality in alternative bivalve prey during a period when the tidal flats of the Dutch Wadden Sea were devoid of mussels. Neth. J. Sea Res. 31:395-406.
- Bij de Vaate, A. 1991. Distribution and aspects of population dynamics of the zebra mussel, <u>Dreissena polymorpha</u> (Pallas, 1771), in the lake IJsselmeer area (the Netherlands). Oecologia 86:40-50.
- Bosveld, A.T.C. and M. Van den Berg. 1994. Effects of polychlorinated biphenyls, dibenzo-p-dioxins, and dibenzofurans on fish-eating birds. Environ. Rev. 2:147-166.
- Boumphrey, R.S., S.J. Harrad, K.C. Jones and D. Osborn. 1993. Polychlorinated biphenyl congener patterns in tissues from a selection of British birds. Arch. Environ. Contam. Toxicol. 25:346-352.
- Braune, B.M. and R.J. Norstrom. 1989. Dynamics of organochlorine compounds in herring gulls: III. Tissue distribution and bioaccumulation in Lake Ontario gulls. Environ. Toxicol. Chem. 8:957-968.
- Brieger, G. and R.D. Hunter. 1993. Uptake and depuration of PCB 77, PCB 169, and hexachlorobenzene by zebra mussels (<u>Dreissena polymorpha</u>). Ecotoxicol. Environ. Safety 26:153-165.
- Cabana, G. and J.B. Rasmussen. 1994. Modelling food chain structure and contaminant bioaccumulation using stable nitrogen isotopes. Nature 372:255-257.

- Carney, S.M. 1992. Species, age and sex identification of ducks using wing plumage. U.S. Department of the Interior, U.S. Fish and Wildlife Service. Washington, D.C. 144 pp.
- Carter D.S. and R.A. Hites. 1992. Fate and transport of Detroit River pollutants throughout Lake Erie. Environ. Sci. Technol. 26:1333-1341.
- Cleven, E.J. and P. Frenzel. 1993. Population dynamics and production of <u>Dreissena polymorpha</u> (Pallas) in River Seerhein, the outlet of Lake Constance (Obersee). Arch. Hydrobiol. 127:395-407.
- Connolly, P. and C.J. Pederson. 1988. A thermodynamic-based evaluation of organic chemical accumulation in aquatic organisms. Environ. Sci. Technol. 22:99-103.
- Custer, T.W. and G.H. Heinz. 1980. Reproductive success and nest attentiveness of mallard ducks fed arochlor 1254. Environ. Poll. 21:313-318.
- Davis, T.E. and R.M. Erwin. 1982. Potential impacts of extended winter navigation upon migratory birds of the Upper U.S. Great Lakes. FWS/OBS-82/51 and U.S. Army Corps of Engineers Tech. Rep. 372 pg.
- Day, R.W. and G.P. Quinn. 1989. Comparisons of treatments after an analysis of variance in ecology. Ecol. Monogr. 59:433-463.
- de Kock, W.C. and C.T. Bowmer. 1993. Bioaccumulation, biological effects, and food chain transfer of contaminants in the zebra mussel (<u>Dreissena</u> <u>polymorpha</u>). pp. 503-533 in T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels: Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.
- Dirksen, S., T.J. Boudewijn, L.K.Slager, R.G. Mes, M.J.M. van Schaick and P. de Voogt. 1995. Reduced breeding success of cormorants (<u>Phalacrocorax carbo</u> <u>sinensis</u>) in relation to persistent organochlorine pollution of aquatic habitats in the Netherlands. Environ. Pollut. 88:119-132.

- Dobos, R.Z., D.S. Painter and A. Murdoch. 1990. Contaminants in wildlife utilizing confined disposal facilities. Int. J. Environ. Pollut. 1:73-86.
- Doherty, F.G., D.W. Evans and E.F. Neuhauser. 1993. An assessment of total and leachable contaminants in zebra mussels (<u>Dreissena polymorpha</u>) from Lake Erie. Ecotoxicol. Environ. Safety 25:328-340.
- Draulans, D. 1982. Foraging and size selection of mussels by the tufted duck, <u>Avthya fuligula</u>. J. Anim. Ecol. 51:943-956.

Ľ,

- Drobney, R.D., J.J. Jones and S.M. Noseworthy. 1982. The effects of winter navigation on waterfowl and benthic communities. Final report to the U.S.
  Fish and Wildlife Service, Grant DOI-C-14-16-009, Patuxent Wildlife Research Center, Laurel, Maryland.
- Duursma, E.K., J. Niewenhuize and J.M. van Liere. 1984. Organochlorine contamination of the Dutch delta region as 'watched' by mussels. Wat. Sci. Tech. 16:619-622.
- Einarsson, A. and M.L. Magnusdottir. 1993. The effect of sediment dredging on the distribution of diving ducks at Lake Myvatn, Iceland. Biological Conservation 66:55-60.
- Evans, M.S., G.E. Noguchi and C.P. Rice. 1991. The biomagnification of polychlorinated biphenyls, toxaphene, and DDT compounds in a Lake Michigan offshore food web. Arch. Environ. Contam. Toxicol. 20:87-93.
- Faldborg, K., K.T. Jensen and L. Maagaard. 1994. Dynamics, growth, secondary production and elimination by waterfowl of an intertidal population of <u>Mytilus</u> <u>edulis</u>. Ophelia Suppl. 6:187-200.
- Farrington, J.W., E.D. Goldberg, R.W. Risebrough, J.H. Martin and V.T. Bowen.
  1983. U.S. "Mussel Watch" 1976-1978: An overview of the trace-metal, DDE,
  PCB, hydrocarbon, and artificial radionuclide data. Environ. Sci. Technol.
  17:490-498.

- Fisher, S.W., D.C. Gossiaux, K.A. Bruner and P.F. Landrum. 1993. Investigations of the toxicokinetics of hydrophobic contaminants in the zebra mussel (<u>Dreissena polymorpha</u>). pp. 465-489 in T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels: Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.
- Foley, R.E. 1992. Organochlorine residues in New York waterfowl harvested by hunters in 1983-1984. Environ. Monit. Assess. 21:37-48.
- Forsyth, D.J., P.A. Martin, K.D. De Smet and M.E. Riske. 1994. Organochlorine contaminants and eggshell thinning in grebes from prairie Canada. Environ. Pollut. 85:51-58.
- Fox, A.D., T.A. Jones, R. Singleton and A.D.Q. Agnew. 1994. Food supply and the effects of recreational disturbance on the abundance and distribution of wintering Pochard on a gravel pit complex in southern Britain. Hydrobiologia 279/280:253-261.
- Fox, G.A. 1993. What have biomarkers told us about the effects of contaminants on the health of fish-eating birds in the Great Lakes? The theory and a literature review. J. Great Lakes Res. 19:722-736.
- French, J.R.P. III. 1993. How well can fishes prey on zebra mussels in eastern North America. Fisheries 18:13-19.
- French, J.R.P. III and M.T. Bur. 1992. Predation of the zebra mussel, <u>Dreissena</u> <u>polymorpha</u>, by freshwater drum in western Lake Erie. Pages 453-464 in T.F. Nalepa and D.W. Schloesser (eds.), Zebra mussels: biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.
- Fry, B., W. Brand, F.J. Mersch, K. Tholke and R. Garritt. 1992. Automated analysis system for coupled  $\delta^{13}$ C and  $\delta^{15}$ N measurements. Analyt. Chem. 64:288-291.

- Fry, B. and R.B. Quinone. 1994. Biomass spectra and stable isotope indicators of trophic level in zooplankton of the northwest Atlantic. Mar. Ecol. Prog. Ser. 112:201-204.
- Furlong, E.T., D.S. Carter and R.A. Hites. 1988. Organic contaminants in sediments from the Trenton Channel of the Detroit River, Michigan. J. Great Lakes Res. 14:489-501.
- Gardarsson, A. and A. Einarsson. 1994. Responses of breeding duck populations to changes in food supply. Hydrobiologia 279/280:15-27.
- Gebauer, M.B. and D.V. Weseloh. 1993. Accumulation of organic contaminants in sentinel mallards utilizing confined disposal facilities at Hamilton Harbour, Lake Ontario, Canada. Arch. Environ. Contam. Toxicol. 25:234-243.
- Geisy, J.P., J.P. Ludwig and D.E. Tillitt. 1994. Deformities in birds of the Great Lakes region. Assigning causality. Environ. Sci. Technol. 28:128-135.
- Gere, G. and S. Andrikovics. 1994. Feeding of ducks and their effects on water quality. Hydrobiologia 279/280:157-161.
- Griffiths, R.W., D.W. Schloesser, J.H. Leach and W.P. Kovalak. 1991. Distribution and dispersal of the zebra mussel (<u>Dreissena polymorpha</u>) in the Great Lakes region. Can. J. Fish. Aquat. Sci. 48:1381-1388.
- Griffiths, R.W. 1992. Effects of zebra mussels (<u>Dreissena polymorpha</u>) on the benthic fauna of Lake St. Clair. pp. 415-437 in T.F. Nalepa and D.W.
  Schloesser (eds.), Zebra Mussels: Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.
- Hamilton, D.J. 1992. A method for reconstruction of zebra mussel (<u>Dreissena</u> <u>polymorpha</u>) length from shell fragments. Can. J. Zool. 70:2486-2490.
- Hamilton, D.J., D. Ankney and R.C. Bailey. 1994. Predation of zebra mussels by diving ducks: an exclosure study. Ecology 75:521-531.

- Hamilton, S.K., W.M. Lewis, Jr. and S.J. Sippel. 1992. Energy sources for aquatic animals in the Orinco River floodplain: evidence from stable isotopes. Oecologia 89:324-330.
- Haramis, G.M., D.G. Jorde and C.M. Bunck. 1993. Survival of hatching-year female canvasbacks wintering on Chesapeake Bay. J. Wildl. Manage. 57:763-771.
- Harris, H.J., T.C. Erdman, G.T. Ankley and K.B. Lodge. 1993. Measures of reproductive success and polychlorinated biphenyl residues in eggs and chicks of Forster's Tern on Green Bay, Lake Michigan, Wisconsin-1988. Arch. Environ. Contam. Toxicol. 25:304-314.
- Haseltine, S.D. and R.M. Prouty. 1980. Arochlor 1242 and reproductive success of adult mallards (Anas platyrhynchos). Environ. Res. 23:29-34.
- Hawker, D.W. and D.S. Connell. 1988. Octanol-water partition coefficients of polychlorinated biphenyl congeners. Environ. Sci. Technol. 22:382-387.
- Heath, R.G., J.W. Spann, J.F. Kreitzer and C. Vance. 1972. Effects of polychlorinated biphenyls on birds. In Proc. 15 <sup>th</sup> Int. Ornithol. Congress, pp. 475-485.
- Hebert, C.E., G.D. Haffner, I.M. Weis, R. Lazar and L. Montour. 1990.Organochlorine contaminants in duck populations of Walpole Island. J. Great Lakes Res. 16:21-26.
- Hebert, P.D.N., B.W. Muncaster and G.L. Mackie. 1989. Ecological and genetic studies on <u>Dreissena polymorpha</u> (Pallas): a new mollusc in the Great Lakes. Can. J. Fish. Aquat. Sci. 46:1587-1591.
- Hesslein, R.H., D.E. Fox and M.S. Capel. 1989. Sulfur, carbon, and nitrogen isotopic composition of fish from the Mackenzie River delta region and other Arctic drainages. Can. Data Rep. Fish. Aquat. Sci. 728:iv + 11 p.

- Hobson, K.A. and R.G. Clark. 1992. Assessing avian diets using stable isotopes I: turnover of <sup>13</sup>C in tissues. Condor 94:181-183.
- Hobson, K.A., J.F. Piatt and J. Pitocchelli. 1994. Using stable isotopes to determine seabird trophic relationships. J. Anim. Ecol. 63:768-798.
- Hoekstra J.A., M.A. Vaal, J. Notenboom and W. Sloof. 1994. Variation in the sensitivity of aquatic species to toxicants. Bull. Environ. Contam. Toxicol. 53:98-105.
- Holland, R.E. 1993. Changes in planktonic diatoms and water transparency in Hatchery Bay, Bass Island area, western Lake Erie since the establishment of the zebra mussel. J. Great Lakes Res. 19: 717-624.
- Ikemoto, Y., K. Motoba and T. Suzuki. 1992. Quantitative structure-activity relationships of nonspecific and specific toxicants in several organism species. Environ. Toxicol. Chem. 11:931-939.
- Jorde, D.G., G.M. Haramis, C.M. Bunck and G.W. Pendleton. 1995. Effects of diet on rate of body mass gain by wintering canvasbacks. J. Wildl. Manage. 59:31-39.
- Junger, M. and D. Planas. 1993. Alteration of trophic interactions between periphyton and invertebrates in an acidified stream: a stable carbon isotope study. Hydrobiologia 262:97-107.
- Kaiser, K.L.E. 1978. The rise and fall of mirex. Environ. Sci. Technol. 12:520-528.
- Kauss, P.B. and Y.S. Hamdy. 1985. Biological monitoring of organochlorine contaminants in the St. Clair and Detroit Rivers using introduced clams <u>Elliptic</u> <u>complanatus</u>. J. Great Lakes Res. 11:247-263.
- Keough, J.R. 1994. Understanding Great Lakes food webs using stable isotope signatures. Great Lakes Wetlands 5:1-10.

- Kidd, K.A., D.W. Schindler, R.H. Hesslein and D.C.G. Muir. 1995. Correlation between stable nitrogen isotope ratios and concentrations of organochlorines in biota from a freshwater food web. Sci. Total Environ. 160/161:381-390.
- Kim, K.S., M.J. Pastel, J.S. Kim and W.B. Stone. 1984. Levels of polychlorinated biphenyls, DDE, and mirex in waterfowl collected in New York State, 1979-1980. Arch. Environ. Contam. Toxicol. 13:373-381.
- Koslowski, S.E., C.D. Metcalfe, R. Lazar and G.D. Haffner. 1994. The distribution of 42 PCBs, including three coplanar congeners, in the food web of the western basin of Lake Erie. J. Great Lakes Res. 20:260-270.
- Kovats, Z.E. and J.J.H. Ciborowski. 1993. Organochlorine contaminant concentrations in caddisfly adults (Trichoptera) collected from Great Lakes connecting channels. Environ. Monit. and Assess. 27:135-158.
- Kreis, R.G., Jr., M.D. Mullin, R. Rossman and L.L. Wallace. 1991. Organic contaminant and heavy metal concentrations in zebra mussel tissue from western Lake Erie. 2nd International Zebra Mussel Research Conference, November 19-22, Rochester, N.Y.
- Kraak, M.H.S., M.C.T. Scholten, W.H.M. Peeters and W.C. de Kock. 1991.
  Biomonitoring of heavy metals in the western European rivers Rhine and
  Meuse using the freshwater mussel <u>Dreissena polymorpha</u>. Environ. Pollut.
  74:101-114.
- Kraak, M.H.S., Y.A. Wink, S.C. Stuijfzand, M.C. Buckert-de Jong, C. J. de Groot and W. Admiraal. 1994. Chronic ecotoxicology of Zn and Pb to the zebra mussel <u>Dreissena polymorpha</u>. Aquat. Toxicol. 30:77-89.
- Kubiak, T.J., H.J. Harris, L.M. Smith, T.R. Schwartz, D.L. Stalling, J.A. Trick, L.
  Sileo, D.E. Docherty and T.C. Erdman. 1989. Microcontaminants and
  reproductive impairment of the Forster's tern on Green Bay, Lake Michigan 1983. Arch. Environ. Contam. Toxicol. 18:706-727.

- Landrum, P.F., D.C. Gossiaux, S.W. Fisher and K.A. Bruner. 1990. The role of zebra mussels in contaminant cycling in the Great Lakes. 1st International
  Zebra Mussel Research Conference, December 5-7, Ohio State University, Ohio.
- Lazar, R., R.C. Edwards, C.D. Metcalfe, F.A.P.C. Gobas and G.D. Haffner. 1992. A simple, novel method for the quantitative analysis of coplanar polychlorinated biphenyls in the environment. Chemosphere 25:493-504.
- Leach, J.H. 1992. Impacts of the zebra mussel (<u>Dreissena polymorpha</u>) on water quality and fish spawning reefs in western Lake Erie. pp. 381-397 in T.F. Nalepa and D.W. Schloesser (eds.), Zebra Mussels: Biology, impacts, and control. Lewis Publishers, Boca Raton, Florida.
- Lovvorn, J.R. 1989. Distributional responses of canvasback ducks to weather and habitat change. J. Applied Ecol. 26:113-130
- MacDonald, C.R., C.D. Metcalfe, G.C. Balch and T.L. Metcalfe. 1993. Distribution of PCB congeners in seven lake systems: interactions between sediment and food-web transport. Environ. Toxicol. Chem. 12:1991-2003.
- MacIsaac, H.J. 1994. Size selective predation on zebra mussels (<u>Dreissena</u> <u>polymorpha</u>) by crayfish (<u>Orconectes propinquus</u>). J. North Amer. Benth. Soc. 13:206-216.
- MacIsaac, H.J. 1996. Potential biotic and abiotic effects of zebra mussels on the inland waterways of North America. Amer. Zool. (in press).
- Mackie G.L. 1991. Biology of the exotic zebra mussel, <u>Dreissena polymorpha</u>, in relation to native bivalves and its potential impact in Lake St. Clair. Hydrobiologia 219:251-268.
- Marvin, C.H., B.E. McCarry and D.W. Bryant. 1994. Determination and genotoxicity of polycyclic aromatic hydrocarbons isolated from <u>Dreissena</u>

polymorpha (zebra mussels) from Hamilton Harbour. J. Great Lakes Res. 20:523-530.

- McCullough, G.B. 1981. Migrant waterfowl utilization of the Lake Erie shore, Ontario, near the Nanticoke industrial development. J. Great Lakes Res. 7:117-122.
- Mersch J., A. Jeanjean, H. Spor and J.C. Pihan. 1992. The freshwater mussel <u>Dreissena polymorpha</u> as a bioindicator for trace metals, organochlorines and radionuclides. pp. 227-244 In D. Neumann and H.A. Jenner (eds.), The zebra mussel <u>Dreissena polymorpha</u> (Limnologie aktuell Band 4). Gustav Fischer Verlag Publishers, New York.
- Mersch, J., E. Morhain and C. Mouvet. 1993. Laboratory accumulation and depuration of copper and cadmium in the freshwater mussel <u>Dreissena</u> <u>polymorpha</u> and the aquatic moss <u>Rhynchostegium riparioides</u>. Chemosphere 27:1475-1485.
- Miles, K.A. and H.M. Ohlendorf. 1993. Environmental contaminants in canvasbacks wintering on San Francisco Bay, California. Calif. Fish and Game 79:28-38.
- Mills, E.L., J.H. Leach, J.T. Carlton and C.L. Secor. 1993. Exotic species in the Great Lakes: a history of biotic crises and anthropogenic introductions. J. Great Lakes Res. 19:1-54.
- Mitchell, C.A. and J. Carlson. 1993. Lesser scaup forage on zebra mussels at Cook Nuclear Plant, Michigan. J. Field Ornithol. 64:219-222.
- Michot, T.C. and A.J. Nault. 1993. Diet differences in redheads from nearshore and offshore zones in Louisiana. J. Wildl. Manage. 57(2):238-244.
- Michot, T.C., E.B. Moser and W. Norling. 1994. Effects of weather and tides on feeding and flock positions of wintering redheads in the Chandeleur Sound, Louisiana. Hydrobiologia 279/280:263-278.

- Murk, A.J., J.H.J. Van den Berg, M. Fellinger, M.J.C. Rozemeijer, C. Swennen, P. Duiven, J.P. Boon, A. Brouwer and J.H. Kceman. 1994. Toxic and biochemical effects of 3,3',4,4'-tetrachlorobiphenyl (CB-77) and Clophen A50 on eider ducklings (Somateria mollissima) in a semi-field experiment. Environ. Pollut. 86:21-30.
- Nalepa, T. 1994. Trends in zebra mussel populations in Saginaw Bay and subsequent changes in water quality. 4th International Zebra Mussel Conference, Madison, WI.
- Nebeker, A.V., W.L. Griffis, T.W. Stutzman, G.S. Schuytema, L.A. Carey and S.M. Scherer. 1992. Effects of aqueous and dietary exposure of dieldrin on survival, growth and bioconcentration in mallard ducklings. Environ. Toxicol. Chem. 11:687-699.
- Nebeker A.V., K.D. Dunn, W.L. Griffis and G.S. Schuytema. 1994. Effects of dieldrin in food on growth and bioaccumulation in mallard ducklings. Arch. Environ. Contam. Toxicol. 26:29-32.
- New York Sea Grant. 1994. North American range of the zebra mussel. In O'Neil, C. (editor), <u>Dreissena</u>! 5:6-7. Published by Zebra Mussel Information Clearinghouse.
- Nicholls, K.H. and G.J. Hopkins. 1993. Recent changes in Lake Erie (north shore) phytoplankton: cumulative impacts of phosphorus loading reductions and the zebra mussel introduction. J. Great Lakes Res. 19:637-647.
- Nummi, P. and H. Poysa. 1993. Habitat associations of ducks during different phases of the breeding season. Ecography 16:319-328.
- Oliver, B.G. and A.J. Niimi. 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. Environ. Sci. Technol. 22:388-397.

- Olszewski, Z. 1978. Reconstruction of the size of mollusc shells in studies on the food of fish. Bulletin de L'Académie Polonaise des Sciences 26:87-91.
- Painter, S. 1990. Ecosystem health and aquatic macrophytes: status and opportunities. In: Proceedings of the Aquatic Ecosystem Health Symposium, July 1990. Waterloo, Ontario.
- Perry, M.C. and F.M. Uhler. 1988. Food habits and distribution of wintering canvasbacks, <u>Avthya valisineria</u>, on Chesapeake Bay. Estuaries 11:57-67.
- Peterson, B.J. and B. Fry. 1987. Stable isotopes in ecosystem studies. Ann. Rev. Ecol. Syst. 18:293-320.
- Peterson, R.E., H.M. Theobald and G.L. Kimmel. 1993. Developmental and reproductive toxicity of dioxins and related compounds: cross-species comparisons. Crit. Rev. Toxicol.. 23:283-335.
- Prince H.H., P.I. Padding and R.W. Knapton. 1992. Waterfowl use of the Laurentian Great Lakes. J. Great Lakes Res. 18:673-699.
- Rasmussen, J.B., D.J. Rowan, D.R.S. Lean and J.H. Carey. 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (<u>Salvelinus</u> <u>namaycush</u>) and other pelagic fish. Can. J. Fish. Aquat. Sci. 47:2030-2038.
- Robertson, A., G.G. Lauenstein and S. Dolvin. 1993. Great Lakes mussel watch:
   organic contaminant levels from Saginaw Bay to western Lake Erie. 36 <sup>th</sup>
   Conference of the International Association of Great Lakes Research, June 4 10. De Pere, Wisconsin.
- Russell, R., R. Lazar and G.D. Haffner. 1995. Biomagnification of organochlorines in Lake Erie white bass. Environ. Toxicol. Chem. 14:1-6.
- Safe, S. 1992. Toxicology, structure-function relationship, and human and environmental health impacts of polychlorinated biphenyls: progress and problems. Environ. Health Perspect. 100:259-268.

- Secor, C.L, E.L. Mills, J. Harshbarger, H.T. Kuntz, W.E. Gutenmann and D.J. Lisk. 1993. Bioaccumulation of toxicants, element and nutrient composition, and soft tissue histology of zebra mussels (<u>Dreissena polymorpha</u>) from New York state waters. Chemosphere 26:1559-1575.
- Sericano, J.L., E.L. Atlas, T.L. Wade and J.M. Brooks. 1990. NOAA's status and trends mussel watch program: chlorinated pesticides and PCBs in oysters (<u>Crassostrea virginica</u>) and sediments from the Gulf of Mexico, 1986-1987. Mar. Environ. Res. 29:161-203.
- Scholten, M.C., E. Foekema, W.C. de Kock and J.M. Marquenie. 1989.
  Reproduction failure in tufted ducks feeding on mussels from polluted lakes.
  In: Proceedings of the 2nd European Symposium on Avian Medicine and Surgery. Utrecht, Holland, 8-11 March 1989.
- Shui, W.Y. and D. Mackay. 1986. A critical review of aqueous solubilities, vapor pressures, Henry's Law constants, and octanol-water partition coefficients of the polychlorinated biphenyls. J. Phys. Chem. Ref. Data. 15(2):931-929.
- Smith, V.E., J.M. Spurr, J.C. Filkins and J.J. Jones. 1985. Organochlorine contaminants of wintering ducks foraging on Detroit River sediments. J. Great Lakes Res. 11:231-246.
- Stanczykowska, A., P. Zyska, A. Dombrowski, H. Kot and E. Zyska. 1990. The distribution of waterfowl in relation to mollusc populations in the man-made Lake Zegrezynskie. Hydrobiologia 191:233-240.
- Stempniewicz, L. 1974. The effect of feeding of the coot (<u>Fulica atra</u>) on the character of the shoals of <u>Dreissena polymorpha</u> Pall. in the Lake Goplo. Prace Limnolog. 34:83-103.
- Struger, J., D.V. Weseloh, D.J. Hallet and P. Mineau. 1985. Organochlorine contaminants in herring gull eggs from the Detroit and Niagara Rivers and

Saginaw Bay (978-1982): contaminant discriminants. J. Great Lakes Res. 11:223-230.

- Suter, V.W. 1982. The influence of waterfowl on populations of zebra mussels (<u>Dreissena polymorpha</u> Pall.) in the Untersee and upper Rhine river (lake of Constance). Schweiz. Z. Hydrol. 44:149-161.
- Suter, W. and M.R. Van Eerden. 1992. Simultaneous mass starvation of wintering diving ducks in Switzerland and the Netherlands: a wrong decision in the right strategy? Ardea 80:229-242.
- Suter, W. 1994. Overwintering waterfowl on Swiss lakes: how are abundance and species richness influenced by trophic status and lake morphology? Hydrobiologia 279/280:1-14.
- Swift, B.L., R.E. Foley and G.R. Batcheller. 1993. Organochlorines in common goldeneyes wintering in New York. Wildl. Soc. Bull. 21:52-56.

Systat. 1992. Version 5.01. Systat Inc., Evanston, IL, USA, 60201.

- Weseloh, D.V. 1986. Preliminary results of contaminant studies in wild and domestic ducks from Walpole Island and Hamiiton Harbour, 1985-86. Canadian Wildlife Service, Burlington, Ontario, Unpubl. Rep.
- Weseloh, D.V., J. Struger and C.E. Hebert. 1994. White pekin ducks (<u>Anas</u> <u>platyrhynchos</u>) as monitors of organochlorine and metal contamination in the Great Lakes. J. Great Lakes Res. 20:277-288.
- White, D.W. and J.T. Seginak. 1994. Dioxins and furans linked to reproductive impairment in wood ducks. J. Wildl. Manage. 58:100-106.
- Winfield, D.K. and I.J. Winfield. 1994. Possible competitive interactions between overwintering tufted duck (<u>Aythya fuligula</u>) and fish populations of Lough Neagh, Northern Ireland: evidence from diet studies. Hydrobiologia 279/280:377-386.

- Wolff, M.S. and A. Schecter. 1991. Accidental exposure of children to polychlorinated biphenyls. Arch. Environ. Contam. Toxicol. 20:449-453.
- Wormington, A. and J.H. Leach. 1992. Concentrations of migrant ducks at Point Pelee National Park, Ontario, in response to invasion of zebra mussels, <u>Dreissena polymorpha</u>. Can. Field Nat. 106:376-380.
- Yamashita, N., S. Tanabe, J.P. Ludwig, H. Kurita, M.E. Ludwig and R. Tatsukawa.
   1993. Embryonic abnormalities and organochlorine contamination in doublecrested cormorants (<u>Phalacrocorax auritus</u>) and Caspian terns (<u>Hydroprogne</u> <u>caspia</u>) from the upper Great Lakes in 1988. Environ. Poll. 79:163-173.
- Zohary, T., J. Erez, M. Gophen, F.I. Berman and M. Stiller. 1994. Seasonality of stable carbon isotopes within the pelagic food web of Lake Kinneret. Limnol. Oceanogr. 39:1030-1043.

Table 1. Groups of waterfowl categories by site, species, and diet (consumer type). Species included are M=mallard, CA=canvasback, RH=redhead, BH=bufflehead, LSC=lesser scaup, and GRS=greater scaup. Consumer type or diet are designated as follows P=plant (macrophyte) or ZM=zebra mussel.

Site	Species-Consumer type	
Big Creek	M-P	
Fighting Island	M-P CA-P RH-P BH-P LSC-F	P LSC-ZM GRS-P GRS-ZM
Lake Erie	BH-ZM	LSC-ZM GRS-ZM

Table 2. Basic description of waterfowl obtained including location collected, species, number, sex, mass, wingspan, length, and date collected.
 Legend: BC=Big Creek, FI=Fighting Island, LE=Lake Erie.

Site	Species	Total number	Total Female	Female Hatching			Male Hatching	Male Adult
One	Opeeles	number	i emaie	Year	Addit	Wate	Year	Auun
		n	n (%)	n	n	n (%)	n	n
BC	mallard	19	3 (16)	2	1	16 (84)	5	11
FI	mallard	7	4 (57)	2	2	3 (43)	2	1
Fl	canvasback	9	4 (44)	0	4	5 (56)	) 4	1
FI	redhead	7	4 (57)	1	3	3 (43)	) 0	3
FI	bufflehead	13	5 (38)	4	1	8 (62)	) 5	3
FI	lesser scaup	11	5 (45)	3	2	6 (55)	) 4	2
Fl	greater scaup	14	8 (57)	7	1	6 (43)	) 4	2
LE	bufflehead	11	7 (64)	4	3	4 (36)	) 3	1
LE	goldeneye	5	3 (60)	1	2	2 (40)	) 1	1
LE	lesser scaup	19	10 (53)	8	2	9 (47	) 3	6
LE	greater scaup	6	4 (67)	3	1	2 (33	) 1	1
	TOTAL	121	57 (47)	35	22	64 (53	) 32	32

<u> </u>						
			<u>Dimensions</u>		Date	Date
Site	Species	Mass	Wingspan	Length	Collected	Collected
		g	cm	cm	from	to
		mean (se)	mean (se)	mean (se)	YYMMDD	YYMMDD
		1000 (00)	04 (1)	61 (1)	001111	021111
BC	mallard	1309 (26)	94 (1)	61 (1)	931111	931111
FI	mallard	1122 (58)	85 (2)	54 (1)	931014	940929
FI	canvasback	1222 (36)	82 (2)	54 (1)	931102	941021
FI	redhead	1064 (53)	80 (1)	50 (1)	931020	941017
Fl	bufflehead	464 (20)	57 (1)	34 (1)	931014	931129
FI	lesser scaup	803 (42)	67 (2)	42 (1)	931012	940927
FI	greater scaup	1019 (34)	72 (1)	42 (1)	931030	931115
	3					
LE	bufflehead	443 (15)	58 (1)	35 (1)	941206	941206
LE	goldeneye	1120 (83)	75 (2)	46 (2)	931125	941206
LE	lesser scaup	985 (30)	73 (0)	44 (0)	931125	940423
LE	greater scaup	1250 (27)	79 (1)	48 (1)	931125	941206

			All Waterfow	ertow					Contar	ninant A	nalyzed	Contaminant Analyzed Waterfowl			
			Sample						Sample	<b>a</b> .					
Species	Site	Diet	Size	Sex	Age	Mass	Wingspan Length	Length	Size	Sex	Age	Mass	Wingspan Length	Length	pidil %
			c	% male % adult	% adult	ß	сш	E	c	% maie % adult	% adult	ŋ	сш	ŝ	
						mean (se) mean (se) mean (se	mean (se)	mean (se)				mean (se) mean (se) mean (se) mean (se)	nean (se) r	nean (se)	mean (se)
Maliard	B	ፈ	19	84	68	1309 (26)	94 (1)	61 (1)	4	50	75	1238 (90)	93 (3)	59 (2)	5.0 (1.4)
Maliard	교	ЪГ	7	43	43	1122 (58)	85 (2)	54 (1)	e	67	100	1067 (137)	88 (2)	53 (2)	3.7 (0.1)
Canvasback	ш	Ы	6	56	56	1222 (36)	82 (2)	54 (1)	Q	20	67	1193 (49)	82 (3)	54 (2)	3.2 (0.2)
Redhead	ū	Ч	7	43	86	1064 (53)	80 (1)	50 (1)	ო	33	67	1085 (114)	79 (3)	50 (2)	3.6 (0.4)
Buttlehead	ш	٦	13	62	31	464 (20)	57 (1)	34 (1)	4	75	0	497 (29)	60 (1)	35 (1)	36 (0.5)
Buttlehead	Щ	ΜZ	11	36	36	443 (15)	58 (1)	35 (1)	S	80	20	479 (21)	60 (1)	37 (1)	6.5 (0.5)
Lesser scaup	Ē	ಗ	2	43	29	791 (58)	66 (3)	43 (1)	4	50	0	861 (47)	69 (2)	44 (1)	3.3 (0.3)
Lesser scaup	Ĩ.	MZ	<del></del>	75	50	825 (63)	69 (1)	42 (1)	ო	100	33	883 (35)	67 (1)	42 (1)	4.9 (1.5)
Lesser scaup	Щ	ZM	19	47	42	985 (30)	73 (0)	44(0)	ø	63	75	1029 (35)	73 (0)	44 (1)	4.9 (0.2)
Greater scaup	ū	ಕ	10	45	18	1030 (48)	73 (2)	43 (1)	4	50	ያ	1028 (58)	71 (2)	43 (1)	3.6 (0.2)
Greater scaup	Ш	ΜZ	e	£	33	1000 (12)	70 (3)	40 (3)	e	33	33	1000 (12)	70 (3)	40 (3)	3.3 (0.2)
	1	i	(	;	ļ				ļ	ę	ļ				

Basic descriptors of all collected waterfowl and contaminant analyzed waterfowl categorized by species, site, and diet including Table 3.

67

Table 4. Pearson correlation coefficients from lipid-normalized liver versus wing concentration regressions for 39 compounds (numbers given denote PCB congeners). Chemical data was obtained from 11 ducks from which both wing and liver were analyzed. Log Kow and slope of the resulting equation are given for each compound.

Compound	n	log Kow	R <sup>2</sup>	slope
QCB	11	5.00	0.72	0.88
dieldrin	9	5.43	0.56	2.70
HCB	11	5.50	0.93	1.00
p,p'-DDE	11	5.65	0.93	0.88
28	11	5.67	0.72	0.86
44	11	5.75	0.85	3.37
52	11	5.84	0.003	0.10
49	11	5.85	0.13	0.55
60	11	6.11	0.14	0.52
70	11	6.20	0.002	0.04
74	11	6.20	0.98	0.75
87	11	6.29	0.69	2.06
97	11	6.29	0.04	-1.20
OCS	11	6.29	0.97	9.16
77	9	6.36	0.04	3.81
101	11	6.38	0.61	1.19
99	11	6.39	0.95	0.95
110	11	6.48	0.81	2.95
151	11	6.64	0.96	1.23
105	11	6.65	0.67	1.47
149	11	6.67	0.97	1.15
129	11	6.73	0.97	1.25
118	11	6.74	0.82	0.82
141	11	6.82	0.88	0.65
138	11	6.83	0.99	1.34
mirex	11	6.89	0.63	0.80
146	11	6.89	0.99	1.03 0.80
153	11	6.92	0.98	1.03
171	11	7.11	0.99 0.99	1.12
174	11	7.11 7.20	0.99	0.97
183	11			1.93
200	11	7.27	0.95	0.85
172	11 11	7.33 7.36	0.99 0.99	1.00
180	11	7.56	0.99	1.01
195 201	11	7.62	0.98	1.04
201	11	7.65	0.98	1.01
203 194	11	7.80	0.98	1.00
206	11	8.09	0.98	0.95
200	I 1	0.09	0.70	0.35

Table 5. Comparisons of ratios of lipid-adjusted concentrations of QCB, p,p'-DDE, OCS, PCBs # 28, 105, 153, 180, 194 and 206 in waterfowl with differing diets or from different sitas. Legend: LSC=lesser scaup, GRS=greater scaup, BH=bufflehead, FIZM/FIPL=[Fighting Island 'mussel-consumer'] + [Fighting Island 'macrophyte-consumer'], LEZM/FIPL=[Lake Erie 'mussel-consumer'] + [Fighting Island 'macrophyte-consumer'], LEZM/FIZM=[Lake Erie 'musselconsumer'] + [Fighting Island 'mussel-consumer']. With exception of DDE, ratios generally increase with K<sub>OW</sub> of the compounds. Greater scaup ratios are higher than lesser scaup ratios. Larger ratios exist between 'musselconsumers' and 'macrophyte-consumers' than between 'musselconsumers' and 'macrophyte-consumers' than between 'mussel-consumers' from different locations.

Comparison	QCB	DDE	28	ocs	105	153	180	194	206
log Kow	5.00	5.65	5.67	6.29	6.65	6.92	7.36	7.80	8.09
BH, LEZM/FIPL	0.9	2.5	1.6	0.9	4.7	6.3	10.6	8.0	4.4
LSC, FIZM/FIPL	1.3	10.4	1.1	1.9	2.5	4.5	4.5	4.1	5.6
LSC, LEZM/FIPL	1.4	10.5	2.6	8.8	5.5	10.2	15.6	15.8	15.4
LSC, LEZM/FIZM	1.1	1.0	2.3	4.6	2.2	2.3	3.4	3.9	2.7
GRS, FIZM/FIPL	1.4	16.1	0.6	38.5	9.2	12.9	23.3	18.2	18.1
GRS, LEZM/FIPL	1.0	22.4	3.5	14.2	24.2	29.4	58.5	43.1	253.7
GRS, LEZM/FIZM	0.7	1.4	6.4	0.4	2.6	2.3	2.5	2.4	14.0

Table 6. Two-way ANOVA results examining the effects of species and diet on the concentration of each log K<sub>OW</sub> representative (QCB, PCBs # 28, 105, 153, 194, and 206) in Fighting Island 'macrophyte' and '<u>Dreissena</u>' consumer scaup (lesser and greater).

Compou	nd Source of variation	d.f	MS	F	P
QCB	SPECIES	1	0.0899	1.8170	>0.10
	DIET	1	0.0311	0.6288	>0.10
	SPECIES x DIET	1	0.0002	0.0049	>0.50
	Error	10	0.0495		
28	SPECIES	1	0.0003	0.0098	>0.50
	DIET	1	0.0276	1.0038	>0.10
	SPECIES x DIET	1	0.0079	0.2889	>0.50
	Error	10	0.0275		
105	SPECIES	1	0.0890	0.3814	>0.50
	DIET	1	1.0190	4.3686	0.0631
	SPECIES x DIET	1	0.0001	0.0006	>0.50
	Error	10	0.2333		
153	SPECIES	i	0.0310	0.0981	>0.50
	DIET	1	1.5544	4.9210	0.0508
	SPECIES x DIET	1	0.0389	0.1233	>0.50
	Error	10	0.3159		
194	SPECIES	1	0.0002	0.0010	>0.50
	DIET	1	1.6628	6.7174	0.0269
	SPECIES x DIET	1	0.0001	0.0006	>0.50
	Error	10	0.2475		
206	SPECIES	1	0.1980	0.9474	>0.10
	DIET	1	2.0262	9.6936	0.0110
	SPECIES x DIET	1	0.0105	0.0502	>0.50
	Error	10	0.2090		

Table 7. Results of two-way ANOVAs examining the effects of collection site and species on the concentration of each log K<sub>OW</sub> representative (QCB, PCBs # 28, 105, 153, 194, and 206) in Fighting Island and Lake Erie '<u>Dreissena</u>-consumer' scaup (lesser and greater)

Compou	nd Source of variation	d.f.	MS	F	P
QCB	SITE	1	0.0050	0.1166	>0.50
000	SPECIES	1	0.0265	0.6180	>0.30
	SITE X SPECIES	1	0.0321	0.7489	>0.10
	Error	, 15	0.0429	0.1400	20.10
			0.0 120		
28	SITE	1	0.7119	16.8977	0.0009
	SPECIES	1	0.0212	0.5020	>0.10
	SITE X SPECIES	1	0.0676	1.6034	>0.10
	Error	15	J.0421		
105	SITE	1	1.0895	8.2076	0.0118
	SPECIES	1	0.0026	0.0194	>0.50
	SITE X SPECIES	1	0.1306	0.9841	>0.10
	Error	15	0.1327		
153	SITE	1	1.5591	8.2062	0.0118
	SPECIES	1	0.0002	0.0010	>0.50
	SITE X SPECIES	1	0.1532	0.8063	>0.10
	Error	15	2.8499		
	0.177				
194	SITE	1	1.8611	12.5612	0.0029
	SPECIES	1	0.0084	0.0568	>0.50
	SITE X SPECIES	1	0.0077	0.0519	>0.50
	Error	15	0.1482		
206	SITE	1	2.0784	9.1462	0.0085
	SPECIES	1	0.0112	0.0494	>0.50
	SITE X SPECIES	1	0.2380	1.0473	>0.10
	Error	15	0.2272		

Table 8. Rotated loadings of components 1, 2, and 3 from a principal component analysis on lipid-adjusted levels of 12 organochlorine compounds in lower Great Lakes' waterfowl collected. Chemicals important in determination of components are highlighted in bold.

	<u> </u>	Loadings	
Chemical	PC 1	PC 2	PC 3
Variance explained	44.5%	18.1%	9.7%
PCB 206	0.91	0.12	0.04
PCB 153	0.88	0.25	0.21
PCB 194	0.88	0.20	0.11
PCB 180	0.88	0.20	0.11
PCB 105	0.77	0.22	0.17
PCB 118	0.82	0.35	0.25
OCS	0.52	0.56	0.01
PCB 174	0.51	0.11	0.28
QCB	0.07	0.93	0.18
НСВ	0.48	0.79	0.01
PCB 28	0.20	0.15	0.91
PCB 149	0.36	0.16	0.24

Reference and location of study	Waterfowf species/tissue	HCB	t-Nonachlor	DDE	Oxychlo, Jane	Dieldrin	PCBs
This study Middle Sister Island, Ontario Middle Sister Island, Ontario Middle Sister Island, Ontario Fighting Island, Detroit R., Ont Fighting Island, Detroit R., Ont	bufflehead/liver greater scaup/liver lesser scaup/liver bufflehead/liver greater scaup/liver lesser scaup/liver	1.4-2.9 (1.8) 0.35-3.4 (1.6) 0.55-1.7 (1.1) 0.54-1.7 (1.1) 0.24-0.81 (0.48) 0.35-0.61 (0.45)	1.3-2.7 (2.3) 0.38-1.1 (0.66) 0.45-1.7 (0.83) 0.25-0.55 (0.39) 0.05-0.07 (0.07) 0.05-0.06 (0.06)	10.7-32.6 (21.0) 7.6-71.5 (22.7) 5.5-32.5 (13.6) 1.3-8.3 (5.2) 0.51-0.84 (0.70) 0.19-1.6 (0.76)	0.68-1.7 (1.0) 0.54-7.8 (3.3) 0.41-3.1 (1.1) 0.58-1.1 (0.80) 0.13-0.22 (0.16) 0.05-0.33 (0.18)		147-308 (237) 120-487 (241) 38.7-241 (133) 9.5-47.6 (26.1) 5.6-7.3 (66) 2.4-20.9 (8.2)
Dobos et al. 1991* Thunder Bay CDF, Ontario	domestic mallards/muscle	ł	I	ļ	1	I	2.6-12.3
Foley 1992 Statewide, New York	mailard/muscle bufftehead/muscle scaup/muscle	(3.1) (7.7) (5.9)	! 1	ND-190 (20) ND-70 (20) ND-30 (20)	(15.0) (34.9) (19.9)	(5.9) (26 4) (17.3)	ND-300 (80) ND-600 (150) ND-500 (130)
KIm et al. 1984 Statewide, New York	mallard/liver bufftehead/liver greater scaup/liver			(24) (5) (43)		111	(520) (75) (1,200)
Miles and Ohlendorf 1993 San Francisco Bay, California	canvasback/carcass	1	(13)	(386)	(11)	(17)	(1,079)
Hebert et al. 1990 <sup>•</sup> Walpole Island, Ontario	non migratory mallards and redheads/liver	(20.0-29.6)	ł	1	1	I	1
Smith et al. 1985* Detroit River, Ontario	lesser and greater scaup, goldeneyeMhole carcass	330-1,700	81-330	480-1,300	-	1	7,600-11,000
Swift et al. 1993 Niagara River, New York	common golder <i>≤yel</i> muscle common goldeneye <i>lf</i> at	0.0-0.0 (0.0) 10-40 (20)	0.0-0.0 (0.0) 10-40 (20)	10-20 (20) 630-970 (780)	0.0-0.0 (0.0) 30-90 (60)	0.0-0.0 (0.0) 100-200 (140)	70-120 (90) 2,470-4,830 (3,450)
Weseloh 1985 <sup>-</sup> St. Clair River, Ontario	mallard, goldeneye, common merganser/muscle	10-276	1-26	21-398	2-22	2-54	225-2,855
Weseloh et al. 1992* Windermere Basin, Ontario Watpole Island, Ontario	pekin ducks/liver pekin ducks/liver	2-18 21-48	4-14 1-2	27-132 8-11	8-139 ND-1	25-73 2-10	1,214-7,555 34-214

Table 9. Comparison of contaminant level results from this study and others. All values given in ug/kg wet weight with mean in parenthesis.

Figure 1. Location of waterfowl collection sites.

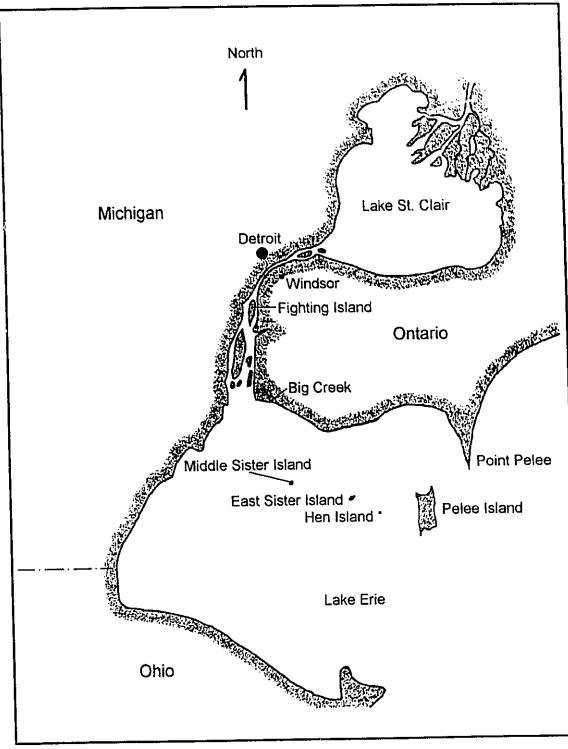


Figure 1.

Figure 2. <u>Dreissena</u> right valve length versus right internal septa length. Measurements were taken only from whole mussels (n=441) found in the esophagus and proventriculus of waterfowl.

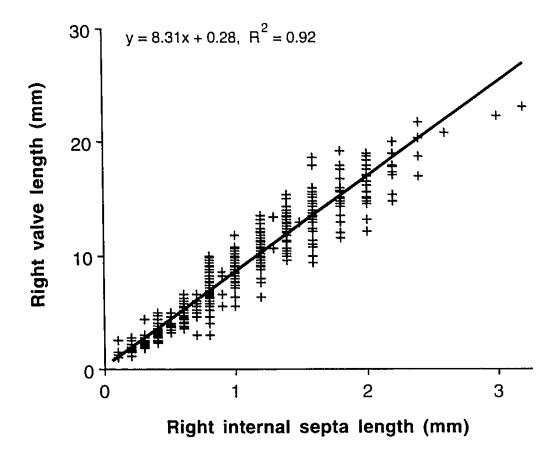


Figure 2.

Figure 3. Percentage dry biomass diet composition (mean ± 1 standard error) of
Big Creek mallard and Fighting Island mallard, canvasback, and redhead.
Virtually only plant material was detected, including <u>Vallisneria americana</u>,
<u>Potamogeton</u> spp., and <u>Elodea canadensis</u>.

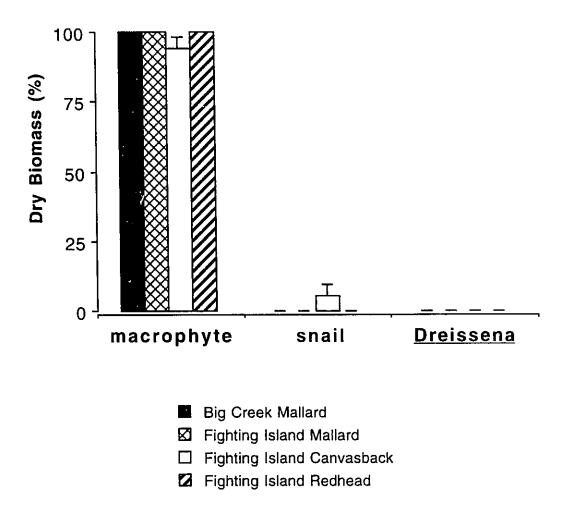


Figure 3.

Figure 4. Percentage dry biomass diet composition (mean ± 1 standard error) of bufflehead and common goldeneye from Fighting Island and Lake Erie.
Fighting Island bufflehead consumed mainly macrophyte, others consumed mainly <u>Dreissena</u>. Lake Erie bufflehead and common goldeneye were the only ducks that consumed amphipod.

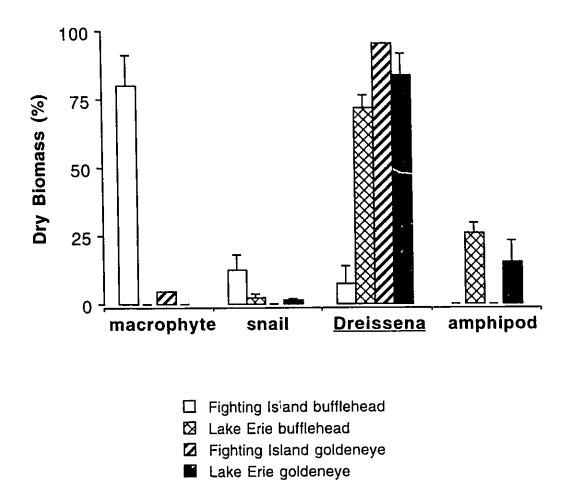
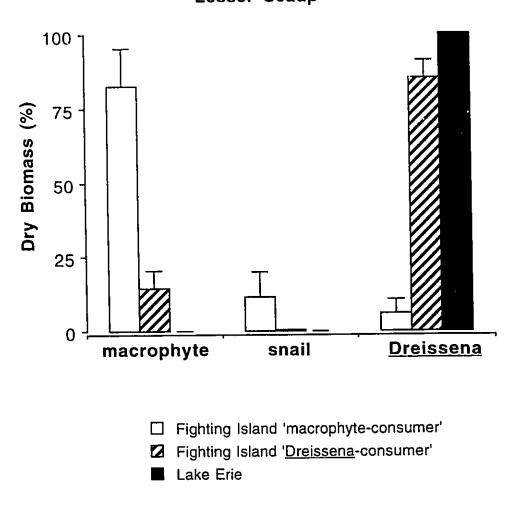


Figure 4.

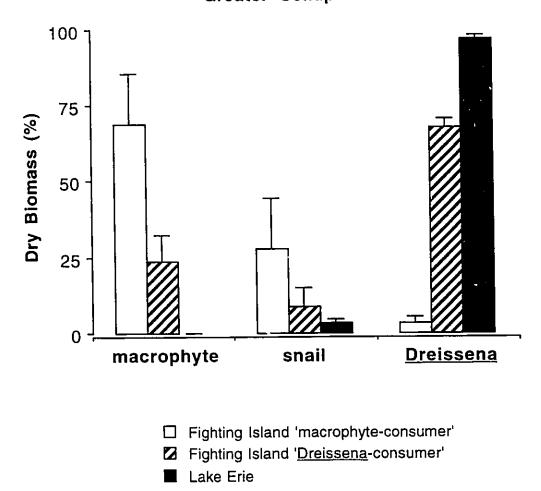
Figure 5. Percentage dry biomass (mean ± 1 standard error) of macrophyte, snail, and <u>Dreissena</u> in the diet of Fighting Island and Lake Erie lesser scaup.
Fighting Island individuals were categorized as 'macrophyte' or '<u>Dreissena</u>' consumers based on diet analysis. Lake Erie scaup consumed the most <u>Dreissena</u>.



Lesser Scaup

Figure 5.

Figure 6. Percentage dry biomass (mean ± 1 standard error) of macrophyte, snail, and <u>Dreissena</u> in the diet of Fighting Island and Lake Erie greater scaup.
Fighting Island individuals were classified as 'macrophyte' or '<u>Dreissena</u>' consumers based on diet analysis. Lake Erie scaup consumed <u>Dreissena</u> to the greatest extent.



Greater Scaup

Figure 6.

Figure 7. Size class distribution of <u>Dreissena</u> consumed by Lake Erie bufflehead, lesser scaup, and greater scaup. On average (mean  $\pm$  1 se, n) bufflehead consumed the smallest mussels (4.6  $\pm$  0.1 mm, n=391), lesser scaup consumed intermediate size mussels (11.1  $\pm$  0.1 mm, n=1,101), and greater scaup consumed the largest mussels (15.3  $\pm$  0.2 mm, n=282). Size distributions were significantly different among all three species of waterfowl (Kolmogorov-Smirnov tests,  $\alpha$ <0.016).

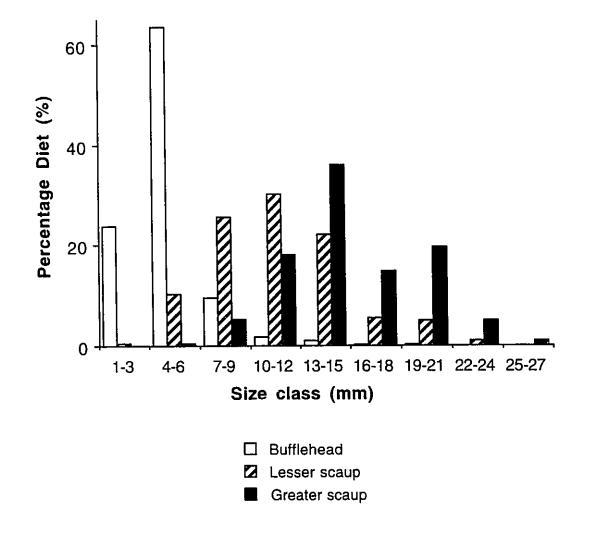


Figure 7.

Figure 8. Contaminant profiles of Big Creek mailard and Fighting Island mallard, redhead, and canvasback. Each profile is based on lipid-adjusted liver tissue means of 39 compounds that appear in the same order as in Appendix A, ranging from low K<sub>OW</sub> on the left to high K<sub>OW</sub> on the right. Error bars represent ± 1 standard error. Open bars from left to right are the log K<sub>OW</sub> representative compounds QCB, PCB # 28, 105, 153, 194, and 206. Only dieldrin and PCB # 138 in Fighting Island mallard and p,p'-DDE and PCB # 153 in canvasback exceed 50 µg kg<sup>-1</sup> lipid. Canvasback are the most contaminated owing to high levels of high K<sub>OW</sub> compounds found in two individuals. See Appendix A for sample sizes used in each profile.

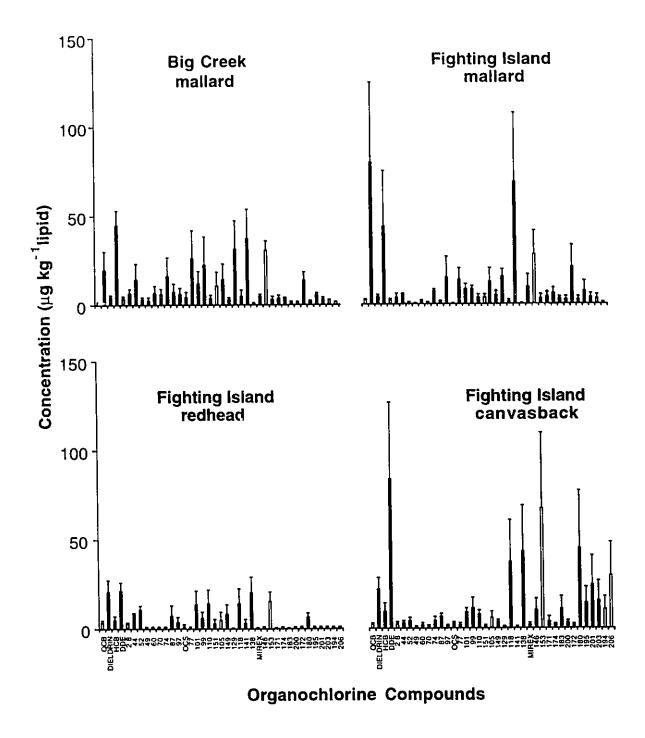
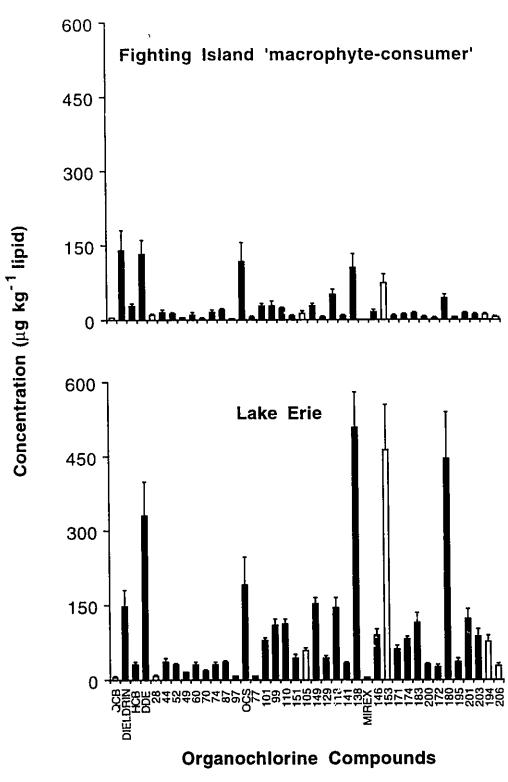


Figure 8.

Figure 9. Lipid-adjusted mean (± 1 standard error) contaminant profiles of liver tissue in bufflehead from Fighting Island and Lake Erie. Order of contaminants and figure legends (K<sub>OW</sub> representatives) as per Figure 8.
Overall Lake Erie bufflehead are significantly more contaminated with the higher K<sub>OW</sub> representatives # 153, 194, 206.



## **Bufflehead**

Figure 9.

Figure 10. Lipid-adjusted mean contaminant profiles of liver tissue in lesser scaup from Fighting Island and Lake Erie. Order of contaminants and figure legends (K<sub>OW</sub> representatives) as per Figure 8. Error bars denote ± 1 standard error. Fighting Island ducks were sorted by major diet component. Higher levels of contaminants were found in 'mussel-consumer' lesser scaup.

۰



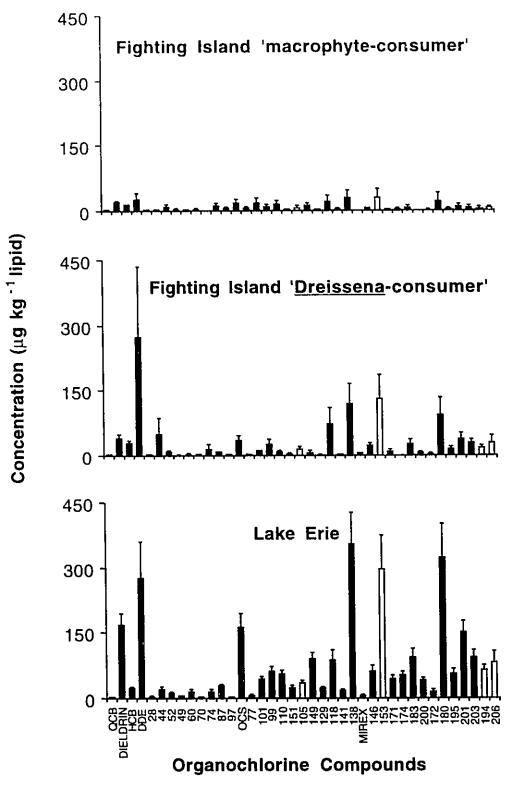


Figure 10.

Figure 11. Lipid-adjusted mean (± 1 standard error) contaminant profiles of liver tissue in greater scaup from Fighting Island and Lake Erie. Order of contaminants and figure legends (K<sub>OW</sub> representatives) as per Figure 8.
Fighting Island ducks were sorted my major diet component. Higher levels of contaminants were found in 'mussel-consumer' greater scaup. Contaminant concentrations detected in Lake Erie greater scaup were the highest found in this study. Standard error bar (not shown) for OCS in Fighting Island
'Dreissena-consumer' is ± 834.

۰.

Greater Scaup

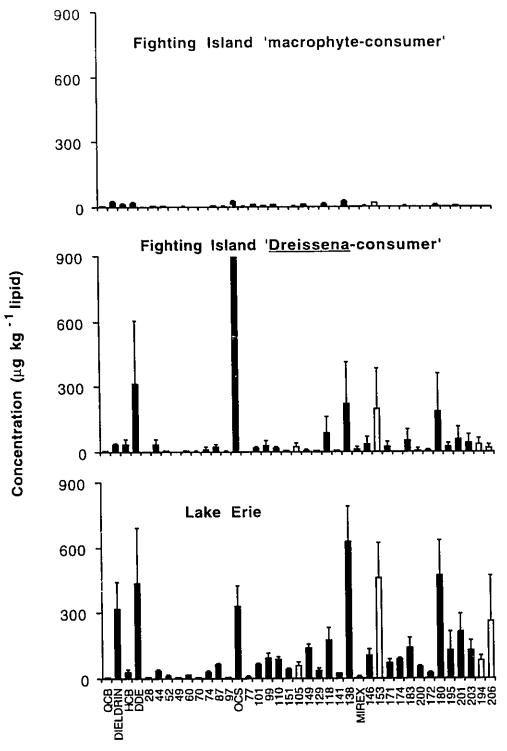






Figure 12. Mean ( $\pm$  1 standard error) lipid-adjusted contaminant profiles of <u>Dreissena</u>, snail and macrophytes. Order of contaminants and figure legends (K<sub>OW</sub> representatives) as per Figure 8. Fighting Island mussels were generally more contaminated than Lake Erie mussels, yet insignificant differences of K<sub>OW</sub> representatives exist. Macrophyte concentrations were very low and are reported on an organic carbon basis. Concentrations in snail are generally lower than those found in <u>Dreissena</u>.

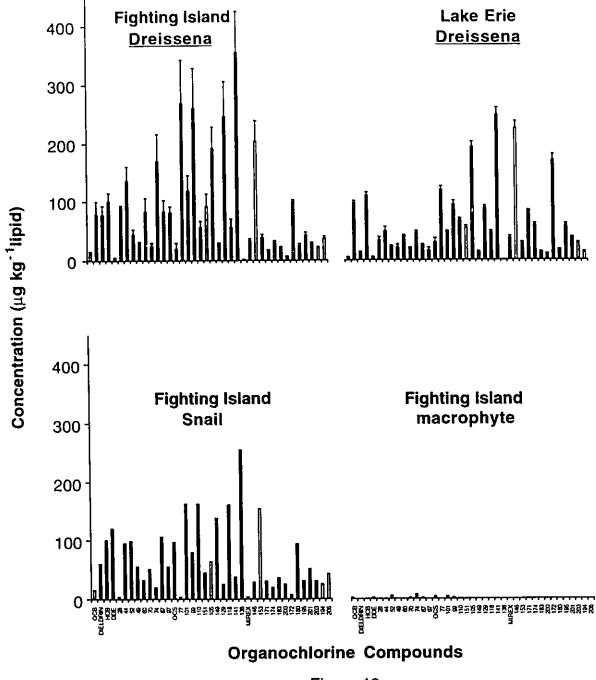


Figure 12.

Figure 13. Biomagnification factors of 33 PCBs in lesser and greater scaup from western Lake Erie that utilized <u>Dreissena</u> as a primary food source. BMFs are based on lipid-adjusted concentrations in waterfowl and <u>Dreissena</u> from Middle Sister Island. Greater scaup (open circles) had consistently higher BMFs than lesser scaup (solid circles). Linear regression yielded equations for lesser scaup of log BMF =  $-3.59 + 0.52 * \log K_{OW}$ , R<sup>2</sup> = 0.54 (dashed line) and for greater scaup of log BMF =  $-3.70 + 0.57 * \log K_{OW}$ , R<sup>2</sup> = 0.54 (solid line).

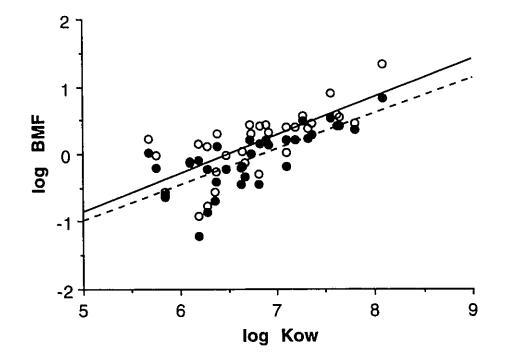
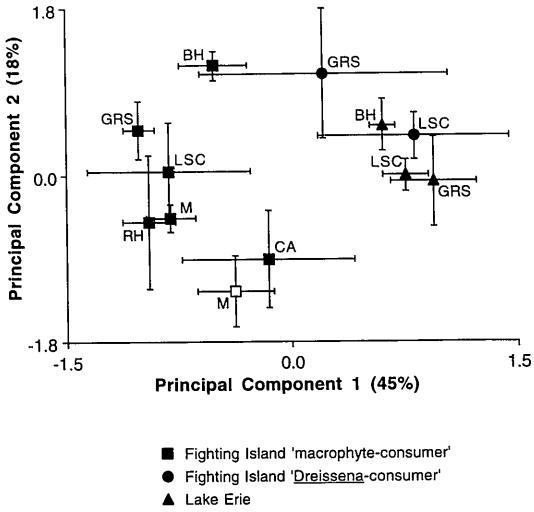


Figure 13.

Figure 14. Factor score plots (mean ± 1 standard error) for waterfowl on PC 1 and PC 2 from the principal component analysis of twelve contaminants in liver tissues. Ducks are plotted by species, location, and diet. Mussel-consumers had higher PC 1 and PC 2 scores and clearly separated from 'macrophyteconsumers'. PC 1 was determined by high K<sub>ow</sub> compounds. Legend: BH=buffiehead; CA=canvasback; GRS=greater scaup; LSC=lesser scaup; M=mallard; RH=redhead.



□ Big Creek

Figure 14.

Figure 15. Mean (± 1 standard error) δ<sup>13</sup>C and δ<sup>15</sup>N isotope signatures of Fighting Island and Lake Erie waterfowl and prey items. Standard error bars not shown are concealed within the symbol chosen. Fighting Island food chain is depicted with squares; open squares are prey items and solid squares are 'macrophyte-consumer' waterfowl. Open circles represent Lake Erie diet items and solid circles Lake Erie waterfowl. Waterfowl legend: BH=bufflehead, CA=canvasback, GRS=greater scaup, LSC=lesser scaup, M=mallard, and RH=redhead.

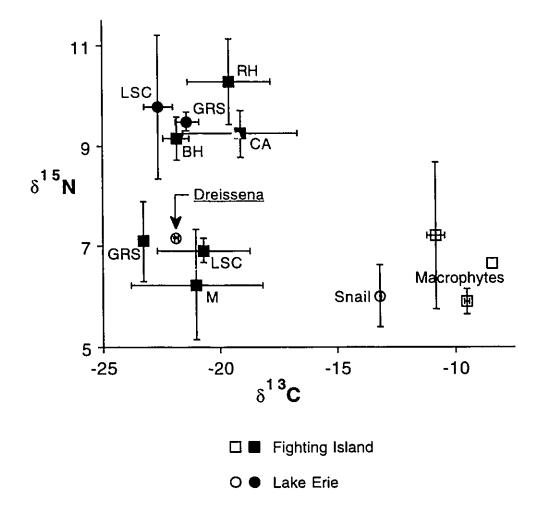


Figure 15.

. •

Figure 16. Relative proportions of 33 PCB congeners in bufflehead, lesser scaup. and greater scaup from both Fighting Island and Lake Erie. Proportions are based on means of single-congener lipid-adjusted liver tissue concentrations divided by the total amount of PCBs in each individual. Error bars are equivalent to 1 standard error. PCB congeners are arranged in order of increasing log K<sub>ow</sub> from left to right. For all three species the 'macrophyteconsumer' waterfowl usually have a higher proportion of lower PCBs (i.e. PCBs # 28 to 101). Mussel-consumers have consistently higher proportions of PCBs # 138 to 206 relative to 'macrophyte-consumers', with Lake Erie 'mussel-consumer' scaup usually having the highest proportion of these PCBs. Compounds in between (i.e. PCBs # 99 to 141) have relative proportions that are equal or are variable among waterfowl groups.

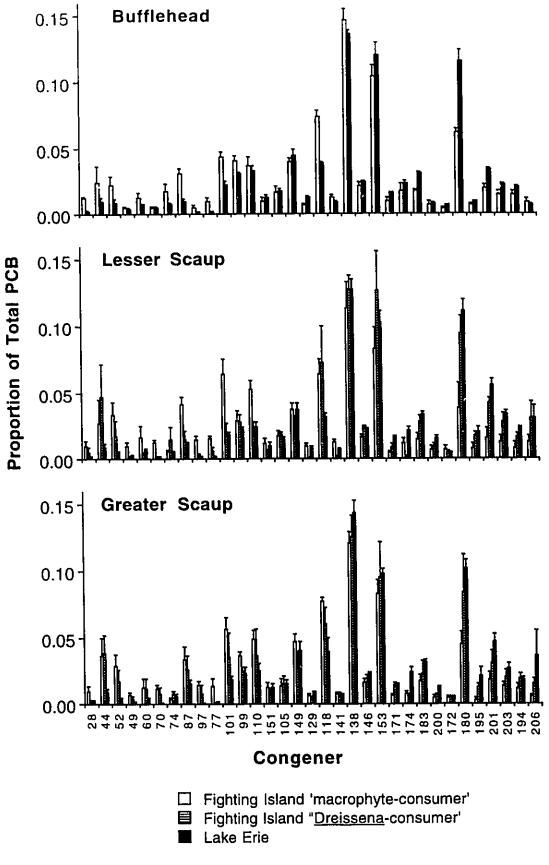


Figure 16.

Figure 17. Greater scaup migration corridors from their breeding grounds in western Alaska to their wintering areas (Taken from Barclay and Zingo 1993).

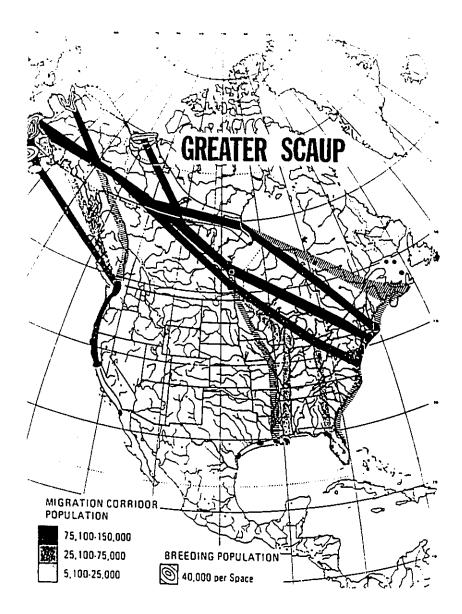


Figure 17.

			diet items		
location		Fighting Island	Fighting Island	Lake Erio	
species		macrophyte	Dreissena	Dreissena	
consumer type			······································		
sample size		6	2	5	
% lipid		40% carbon	1.0 ± 0.1	1.0 ± 0.3	
compound	log Kow				
QCB	5.00	0.2 ± 0.1	16 ± 0.2	3.9 ± 1.2	
DIELDRIN	5.43	ND	80 ± 19	97 ± 3.6	
HCB	5.50	$0.4 \pm 0.1$	78 ± 16	13 ± 1.0	
DDE	5.65	$0.9 \pm 0.1$	100 ± 14	109±5.3	
#28	5.67	ND	4.0 ± 0.3	3.8 ± 0.8	
#44	5.75	0.5 ± 0.4	90 ± 3.2	34 1 3.9	
#52	5.84	$4.0 \pm 1.4$	135 ± 26	50 ± 6.7	
#49	5.85	ND	45 ± 7.4	22 £ 2.8	
#60	6.11	0.1 ± 0.01	31 ± 0.1	21±5.3	
#70	6.20	1.1 ± 0.6	83 ± 22	41 ± 2.2	
#74	6.20	$6.3 \pm 0.2$	$25 \pm 4.3$	19±2.2	
#87	6.29	$0.8 \pm 0.3$	170 ± 45	47 ± 3.6	
#97	6.29	$0.3 \pm 0.1$	82 ± 20	24 t 2.0	
OCS	6.29	2.1 ± 0.6	82 ± 10	15±6.3	
#77	6.36	ND	19±11	30 ± 6.4	
#101	6.38	$2.4 \pm 0.3$	268 ± 75	118 ± 7.4	
#99	6.39	$1.6 \pm 0.3$	$118 \pm 28$	47 ± 2.2	
#110	6.48	$0.4 \pm 0.1$	$260 \pm 69$	93 ± 6.6	
#151	6.64	$0.2 \pm 0.02$	57 ± 10	66 ± 4.2	
#105	6.65	$0.1 \pm 0.01$	93 ± 21	54 ± 3.6	
#149	6.67	$0.3 \pm 0.1$	190 ± 37	193 ± 8.6	
#129	6.73	ND	28 ± 2.8	14 ± 0.6	
#118	6.74	$0.2 \pm 0.1$	245 ± 60	87±4.9	
#141	6.82	$0.2 \pm 0.1$	57 ± 14	46 ± 3.2	
#138	6.83	$0.6 \pm 0.1$	354 ± 71	247 ± 13	
MIREX	6.89	0.1 ± 0.01	$2.2 \pm 0.4$	0,6 ± 0.3	
#146	6.89	$0.2 \pm 0.03$	$34 \pm 4.1$	38 ± 2.3	
#153	6.92	$0.7 \pm 0.03$	<b>203 ± 35</b>	224 ± 13	
#171	7.11	$0.1 \pm 0.03$	38 ± 5.6	28 ± 2.6	
#174	7.11	$0.1 \pm 0.01$	17 ± 1.0	82 ± 3.2	
#183	7.20	$0.4 \pm 0.1$	32 ± 1.7	58 ± 3.8	
#200	7.27	$0.1 \pm 0.01$	22 ± 1.3	14 ± 1.5	
#172	7.33	$0.1 \pm 0.01$	5.5 ± 1.0	9.3 ± 0.7	
#180	7.36	$0.2 \pm 0.04$	99 ± 3.3	169±11	
#195	7.56	0.1 ± 0.01	$24 \pm 4.0$	16 ± 1.3	
#201	7.62	$0.1 \pm 0.01$	43 ± 5.2	58 ± 4.7	
#203	7.65	0.1 ± 0.01	27 ± 2.5	36 ± 3.0	
#194	7.80	0.1 ± 0.01	20 ± 3.2	29 ± 1.5	
#206	8.09	0.1 ± 0.01	37 ± 4.3	12 ± 2.2	
Total PCB		25 ± 2.3	3375 ± 580	2359 ± 9	

Appendix A. Concentrations of lipid normalized organochlorine compounds (mean + tse) in diet items and watertowf collected from Fighting Island and Lake Erie.

----

			····	waterfowl			_
location		Big Creek	Fighting Isl.	Fighting Isl.	Fighting Isl.	Fighting Isl.	Lake Erie
species consumer type		mailard	mallard macrophyte	canvasback macrophyte	redhead macrophyte	bufflehead macrophyte	bufflehead <u>Dreissena</u>
		macrophyte					
sample size		4	3	6	3	4	5
% lipid		5.0 ± 1.4	3.7 ± 0.1	3.2 ± 0.2	3.6 ± 0.4	3.6 ± 0.5	6.5 ± 0.5
compound	log Kow						
QCB	5.00	$1.3 \pm 0.5$	$2.5 \pm 0.3$	2.1 ± 1.0	$3.3 \pm 1.6$	$5.8 \pm 0.5$	$5.4 \pm 1.1$
DIELDRIN	5.43	19 ± 11	83 ± 47	22 ± 6.7	21 ± 6.3	$140 \pm 40$	$146 \pm 35$
нсв	5.50	$4.0 \pm 1.2$	4.1 ± 0.9	9.2 ± 5.2	5.0 ± 2.1	29 ± 3.2	$30 \pm 5.5$
DDE	5.65	45 ± 8.2	45 ± 32	84 ± 43	21 ± 5.1	$133 \pm 28$	331 ± 67
#28	5.67	$3.8 \pm 1.2$	$2.5 \pm 0.5$	2.6 ± 0.8	2.7 ± 1.0	8.9 ± 2.6	7.6 ± 2.2
H44	5.75	$6.2 \pm 2.5$	$3.5 \pm 2.7$	3.2 ± 1.0	$8.4 \pm 0.7$	14 ± 4.9	37 ± 5.9
#52	5.84	14 ± 8.6	$5.4 \pm 0.4$	4.3 ± 1.5	10 ± 2.2	12 ± 1.9	$29 \pm 4.7$
#49	5.85	2.9 ± 1.1	$0.9 \pm 0.2$	$1.0 \pm 0.4$	$1.2 \pm 0.2$	$3.9 \pm 1.1$	$14 \pm 2.1$
#60	6.11	$2.3 \pm 1.8$	$0.7 \pm 0.1$	$2.0 \pm 1.1$	$0.9 \pm 0.3$	10 ± 4.6	31 ± 4.7
#70	6.20	6.6 ± 4.2	1.6 ± 0.7	$1.2 \pm 0.4$	$0.9 \pm 0.2$	$3.6 \pm 0.8$	18 ± 3.2
#74	6.20	5.6 ± 3.2	$0.8 \pm 0.2$	$3.9 \pm 2.7$	$1.0 \pm 0.1$	$14 \pm 6.8$	31 ± 4.3
#87	6.29	16 ± 10	7.5 ± 1.2	$6.4 \pm 2.1$	6.8 ± 6.2	$20 \pm 2.8$	36 ± 2.6
#97	6.29	6.8 ± 5.1	1.1 ± 0.6	$1.4 \pm 0.4$	3.7 ± 2.6	$2.5 \pm 0.8$	6.5 ± 1.1
OCS	6.29	5.6 ± 3.6	15 ± 12	$2.8 \pm 0.8$	$1.3 \pm 0.9$	$116 \pm 38$	191 ± 57
#77	6.36	4.3 ± 2.9	0.4 ± 0.1	$2.0 \pm 0.9$	$1.0 \pm 0.2$	$6.1 \pm 0.4$	8.2 ± 0.5
#101	6.38	26 ±16	$14 \pm 6.1$	8.7 ± 2.6	$13 \pm 8.0$	29 ± 4.5	78 ± 7.1
#99	6.39	12 ± 6.7	9.0 ± 3.0	11 ± 5.8	$6.1 \pm 3.2$	29 ± 8.3	$110 \pm 11$
#110	6.48	22 ± 16	8.6 ± 2.2	7.7 ± 2.2	14 ± 7.8	$23 \pm 3.9$	113 ± 10
#151	6.64	3.7 ±1.8	3.6 ± 2.0	$1.4 \pm 0.2$	2.8 ± 2.3	6.9 ± 2.3	44 ± 5.4
#105	6.65	11 ± 7.7	$3.4 \pm 2.1$	5.6 ± 4.0	5.0 ± 4.5	13 ± 5.0	59 ± 4.3
#149	6.67	14 ± 8.9	13 ± 7.7	3.6 ± 1.2	8.2 ± 5.6	27 ± 5.9	$154 \pm 10$
#129	6.73	3.0 ± 1.1	4.7 ± 3.2	1.2 ± 0.1	$0.5 \pm 0.1$	$5.0 \pm 1.7$	44 ± 3.3
#118	6.74	31 ± 16	$16 \pm 3.8$	37 ± 24	14 ± 8.3	$50 \pm 11$	$145 \pm 22$
#141	6.82	4.9± 3.2	$1.5 \pm 0.6$	1.0 ± 0.3	$2.9 \pm 2.4$	8.1 ± 2.3	33 ± 2.8
#138	6.83	37 ± 16	71 ± 40	43 ± 26	20 ± 8.9	105 ± 28	509 ± 71
MIREX	6.89	$0.8 \pm 0.4$	$0.6 \pm 0.2$	2.0 ± 0.7	$0.4 \pm 0.04$	$1.0 \pm 0.2$	5.4 ± 0.9
#146	6.89	4.7 ± 1.3	10 ± 6.9	$10 \pm 6.7$	0.8 ± 0.1	$16 \pm 5.4$	89 ± 13
#153	6.92	30 ± 5.5	29 ± 14	67 ± 42	16 ± 5.2	73 ± 19	462 ± 93
#171	7.11	$3.2 \pm 1.3$	$2.9 \pm 2.5$	3.7 ± 2.9	$0.5 \pm 0.2$	7.8 ± 2.7	60 ± 8.6
#174	7.11	3.4 ± 1.6	$4.4 \pm 2.7$	$1.8 \pm 0.3$	i.0 ± 0.3	11 ± 2.5	81 ± 5.2
#183	7.20	$3.6 \pm 0.6$	$5.8 \pm 3.7$	$11 \pm 7.3$	$0.6 \pm 0.3$	12±3.3	115 ± 20
#200	7.27	1.2 ± 0.6	$2.7 \pm 1.5$	3.0 ± 1.1	1.0 ± 0.3	$5.4 \pm 2.5$	<b>29 ± 2.5</b>
#172	7.33	$1.2 \pm 0.3$	$2.4 \pm 1.5$	1.8 ± 0.5	$0.9 \pm 0.2$	3.0 ± 1.0	26 ± 4.6
#180	7.36	$13 \pm 4.5$	$22 \pm 13$	45 ± 33	6.7 ± 1.9	42 ± 8.9	445 ± 93
#195	7.56	$2.1 \pm 0.1$	$2.3 \pm 1.7$	14 ± 8.7	$0.8 \pm 0.3$	4.6 ± 1.1	37 ± 6.2
#201	7.62	5.3 ± 1.0	$7.8 \pm 5.9$	24 ± 17	$1.1 \pm 0.3$	$13 \pm 2.8$	123 ± 19
#203	7.65	$3.0 \pm 1.0$ $3.0 \pm 1.2$	$3.5 \pm 2.2$	$15 \pm 11$	$0.8 \pm 0.3$	9.7 ± 2.0	85 ± 15
#203 #194	7.80	$3.0 \pm 0.2$	$3.0 \pm 2.2$	$10 \pm 7.4$	$0.7 \pm 0.3$	9.4 ± 2.2	75 ± 15
#206	8.09	$1.5 \pm 0.4$	$0.9 \pm 0.3$	29 ± 19	$0.9 \pm 0.3$	$6.3 \pm 1.5$	28 ± 5.0
Total PCB		347 ± 149	330 ± 172	443 ± 238	179 ± 75	693 ± 154	3722 ± 4

Appendix A continued	Concentrations of lipid normalized organochlorine compounds (mean ± 1se) in diet items	
and waterlowl collected from Fighting Island and Lake Erie.		

				waterfowl			
location	<u> </u>	Fighting Isl.	Fighting Isl.	Fighting Isl.	Fighting Isl.	Lake Erio	Lake Erie
species consumer type sample size		lesser scaup			greater scaup <u>Dreissena</u> 3		
		macrophyte	macrophyte			Dreissena	
		4	4			8	
% lipid		3.3 ± 0.3	$3.6 \pm 0.2$	4.9 ± 1.5	3.3 ± 0.2	4.9±0.2	5.5 ± 0.5
compound	log Kow						
QCB	5.00	$2.3 \pm 0.8$	$3.5 \pm 0.9$	$3.0 \pm 1.2$	4.9 ± 2.0	3.3 L 0.5	3.6 ± 1.0
DIELDRIN	5.43	$19 \pm 3.4$	$24 \pm 6.2$	42 ± 8.7	34 ± 3.7	169 ± 25	322 ± 117
нсв	5.50	13 ± 0.8	13 ± 2.5	$30 \pm 3.7$	36 ± 24	23 ± 2.8	30 ± 11
DDE	5.65	26 ± 13	20 ± 2.6	274 ± 163	$314 \pm 290$	277 ± 83	437 ± 253
#28	5.67	1.5 ± 0.3	1.8 ± 0.4	$1.7 \pm 1.1$	$1.0 \pm 0.2$	3.9 ± 0.9	$6.4 \pm 1.2$
#44	5.75	<b>2.7</b> ± 1.1	6.1 ± 2.2	50 ± 38	35 ± 22	21 ± 3.4	33 t 6.1
#52	5.84	9.8 ± 5.9	$5.9 \pm 2.1$	8.6 ± 2.2	5.6 ± 2.5	12 ± 1.3	14 ± 2.5
#49	5.85	2.8 ± 1.6	$1.3 \pm 0.5$	$1.1 \pm 0.6$	$2.1 \pm 0.8$	$5.3 \pm 1.0$	5.6±0.4
#60	6.11	2.6 ± 1.6	$2.5 \pm 1.6$	4.1 ± 2.0	4.8 ± 1.9	$15 \pm 4.0$	16 ± 2.1
#70	6.20	$3.5 \pm 2.1$	$2.1 \pm 0.6$	$1.6 \pm 0.8$	2.7 ± 1.5	$2.5 \pm 0.6$	4.8 ± 0.7
#74	6.20	1.1 ± 0.3	0.7 ± 0.1	15 ± 11	13 ± 11	16 ± 5.4	27 t 10
#87	6.29	12 ± 6.8	6.5 ± 2.2	8.4 ± 1.4	$23 \pm 13$	28 ± 3.3	61±11
#97	6.29	$4.8 \pm 3.2$	$2.8 \pm 0.8$	2.5 ± 0.9	2.6 ± 2.1	$3.5 \pm 0.4$	4.1 ± 1.0
ocs	6.29	18 ± 7.2	$23 \pm 8.1$	35 ± 12	892 ± 834	$163 \pm 32$	329 ± 97
#77	6.36	4.7 ± 3.0	$2.8 \pm 1.4$	$3.6 \pm 0.7$	1.5 ± 1.1	6.0 ± 1.4	8.6 ± 1.1
#101	6.38	18 ± 10	$11 \pm 2.5$	11 ± 1.6	18 ± 6.2	$45 \pm 4.5$	66±5.9
#99	6.39	8.3 ± 4.9	6.6 ± 0.7	27 ± 11	31 ± 23	60 ± 13	95 ± 22
#110	6.48	15 ± 9.1	9.2 ± 1.7	9.1 ± 1.7	$15 \pm 6.0$	55 ± 7.7	89±7.9
#151	6.64	2.6 ± 1.4	$2.2 \pm 0.6$	3.9 ± 2.2	5.1 ± 2.3	24 ± 4.0	42 ± 6.1
#105	6.65	$6.4 \pm 4.6$	24 ± 1.0	16 ± 5.2	22 ± 18	35 ± 5.6	59 ± 14
#149	6.67	11 ± 6.8	8.8 ± 1.7	6.6 ± 4.0	7.5 ± 4.5	90 ± 15	141 ± 14
#129	6.73	$2.6 \pm 1.5$	$1.4 \pm 0.3$	1.4 ± 0.5	4.5 ± 2.7	23 ± 3.9	38 ± 7.6
#118	6.74	21 ± 13	14 ± 1.8	72 ± 37	90 ± 72	87 ± 23	172 ± 60
#141	6.82	3.7 ± 2.2	$1.5 \pm 0.4$	$1.6 \pm 0.7$	3.2 ± 1.2	16 ± 2.8	24 ± 2.5
#138	6.83	$30 \pm 17$	23 ± 3.6	119 ± 46	221 ± 191	355 ± 73	624 ± 166
MIREX	6.89	0.6 ± 0.1	0.8 ± 0.1	5.0 ± 2.2	12 ± 9.4	6.4 ± 1.1	7.3±3.1
#146	6.89	$4.4 \pm 2.6$	$2.9 \pm 0.6$	22 ± 7.9	37 ± 34	62 ± 14	103 ± 33
#153	6.92	29 ± 20	16 ± 2.9	131 ± 55	200 ± 182	298 ± 77	457 ± 165
#171	7.11	2.1 ± 1.7	$1.2 \pm 0.1$	9.0 ± 4.1	24 ± 21	44 ± 8.1	68 ± 20
#174	7.11	3.0 ± 1.9	$1.6 \pm 0.5$	0.7 ± 0.2	1.3 ± 0.4	52 ± 9.6	86 ± 8.2
#183	7.20	$6.5 \pm 5.6$	$2.9 \pm 0.6$	26 ± 11	53 ± 49	94 ± 21	141 ± 47
#200	7,27	$1.0 \pm 0.3$	$0.8 \pm 0.3$	6.8 ± 1.9	8.5 ± 6.7	41 ± 7.2	50 ± 10
#172	7.33	$1.3 \pm 0.6$	$0.9 \pm 0.2$	$3.9 \pm 1.3$	6.7 ± 5.6	16 ± 3.5	22 ± 4.7
#180	7.36	21 ± 19	$8.0 \pm 1.3$	93 ± 41	187 ± 173	322 ± 80	470 ± 162
#195	7.56	2.7 ± 2.0	$0.6 \pm 0.2$	15 ± 5.6	$23 \pm 20$	54 ± 12	128 ± 84
#201	7.62	8.2 ± 7.6	$3.1 \pm 1.0$	$39 \pm 14$	60 ± 55	150 ± 27	216 ± 78
#203	7.65	5.7 ± 5.1	$2.2 \pm 0.5$	$28 \pm 11$	41 ± 38	93 ± 18	128 ± 49
#203 #194	7.80	$3.7 \pm 3.1$ $4.0 \pm 3.6$	$1.8 \pm 0.5$	16 ± 6.9	$33 \pm 29$	$63 \pm 11$	79 ± 25
#194 #206	8.09	$4.0 \pm 3.0$ 5.2 ± 4.5	$1.0 \pm 0.2$	29 ± 17	19 ± 15	80 ± 27	260 ± 208
Total PCB		300 ± 190	185 ± 21	914 ± 317	1462 ± 1191	2734 ± 483	4464 ± 136

Appendix A continued.	Concentrations of lipid normalized organochlorine compounds (mean + 1se) in diet items		
and waterlowl collected from Fighting Island and Lake Erie.			

## VITA AUCTORIS

Name:	Edward John Mazak
Date of Birth:	August 20, 1964
Place of Birth:	Windsor, Ontario
Education:	Sandwich Secondary High School LaSalle, Ontario 1980-1984
	University of Windsor Windsor, Ontario 1985-1990 Hons. B. Sc.
	University of Windsor Windsor, Ontario 1993-1995 M. Sc.