SPATIALLY DISTRIBUTED BIOACCUMULATION RISK ANALYSIS: A GIS-BASED TOOL AND A CASE STUDY OF POLYCHLORINATED BIPHENYLS IN THE GREAT LAKES

BY

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THESIS

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ABSTRACT

This thesis presents a GIS-based tool Arc-BEST (Bioaccumulation Evaluation Screening Tool) to perform spatially distributed bioaccumulation risk analyses. Estimating bioaccumulation risk is important to help predict potentially adverse effects from contaminants on ecosystems and human health, which are key factors in the development of sound public policy.

Arc-BEST is based on the BEST model in the U.S. Army Corps of Engineers BRAMS (Bioaccumulation Risk Assessment Modeling System) software, released in 2012. It predicts concentration of concern contaminants in predators tissues from concentrations in organisms at the bottom of the food chain. It also estimates carcinogenic and non-carcinogenic risks for humans that consume those species. The new tool is easy to use, requires few parameters, and is flexible to modify the food chain structure and exposure scenarios.

The greatest contribution of Arc-BEST is that it enables the automated use of digital spatial data sets, which improves model creation speed and the analysis, comparison and visualization of results. Furthermore, the model was improved to consider up to four trophic levels. The code for Arc-BEST is written in Python, is open-source, and can also be used as a stand-alone model called by other software programs.

In this work Arc-BEST is proposed to be used as part of a screening-level risk assessment process in order to identify hot spots where further studies and monitoring should be performed to ensure humans and ecosystems health. The tool is successfully applied to a case study of PCBs in the Laurentian Great Lakes, where long-term effects of PCBs is performed, based on concentrations in zebra mussels (*Dreissena polymorpha*).

Zebra mussels have a great filtration capacity and high bioconcentration rates, increasing the bioavailability of contaminants for predator species. PCBs concentrations in different-level predators are predicted. Furthermore, health risks for humans that consume sport fish are estimated for different exposure scenarios. The distribution of the risks in the different lakes is analyzed, and critical areas are identified.

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Table of Contents

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 What is Bioaccumulation?

The environment is continuously loaded with man-made organic chemicals and metals released by urban communities and industries. Examples of these chemicals are polychlorinated biphenyls (PCBs), organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), dioxins, and mercury. The ultimate destination for many of these contaminants is the aquatic environment, either due to direct discharges or to hydrologic and atmospheric processes [2]. They can represent a potential risk for human health and for both aquatic and terrestrial ecosystems due to the mechanism of bioaccumulation.

Bioaccumulation is defined as "*the uptake of organic compounds by biota from either water or food. Many toxic organic chemicals attain concentrations in biota several orders of magnitude greater than their aqueous concentrations, and therefore, bioaccumulation poses a serious threat to both the biota of surface waters and the humans that feed on these surface-water species*" [3]. Bioaccumulation happens because the rate of intake in an organism exceeds the removal rate. Besides organic chemicals, some heavy metals also have the capacity to bioaccumulate. Furthermore, sediments can serve both as a sink and reservoir of contaminants, entering the aquatic food web through benthic organisms [4]. Figure 1.1 shows an schematic representation of the links between contaminants generated from human activities and receptors. As it can be observed in this figure, chemicals from different sources, such as industries, cities, and agriculture can end in water bodies, where they can be distributed into the water column and sediments. Then, bioaccumulation of contaminants from these compartments to organisms at the bottom of the trophic chain, and their subsequent transfer through the food web provides an exposure pathway to higher-level predators, such as fish, birds, and mammals.

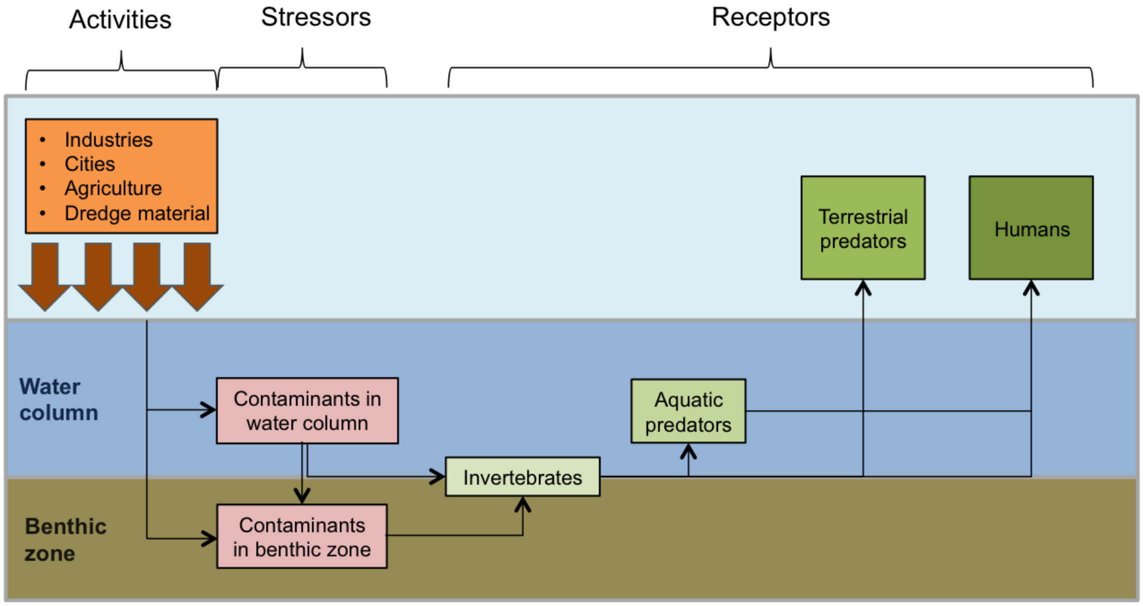

Figure 1.1: Schematic representation of bioaccumulation. Contaminants that are discharged in water bodies are transferred through the trophic web to higher-level predators. (From [1]).

It is important to estimate bioaccumulation of chemicals in aquatic organisms to help predict potentially adverse effects on ecosystems in general, and particularly on high-level predators that consume them [5]. Because humans are at the top of the food chain, the health risks for consuming contaminated species can be magnified.

1.2 Objective and Motivation

This thesis has two main objectives. The first one is to develop a Geographic Information System (GIS)-based tool to calculate bioaccumulation of contaminants in aquatic ecosystems, and estimate health risks for humans that feed on these species. The second objective is to use Arc-BEST in the study of current risks to local aquatic ecosystem and population posed by PCBs in the Great Lakes region of the Midwest.

For the first objective, GIS can add extremely valuable resources to a risk analysis assessment, facilitating the incorporation of social-cultural, economical, and environmental aspects to the study. There are several works that use a GIS-based approach in assessing human and ecological risks due to environmental pollutants. Some examples are Clifford *et. al.* [6], Morra *et. al.* [7], Nadal *et. al.* [8], Liang *et. al.* [9], and Chen *et. al.* [10]. In these studies, GIS has proved to be a very effective tool to manipulate and analyze spatially arrayed data, in order to better analyze the spatial distribution of hazards and generate risk maps. This type of map could be useful in decision-making processes concerning environmental pollutants. On the other hand, the United States Army Corps of Engineers (USACE) and the Environmental Protection Agency (USEPA) released in 2012 the *Bioaccumulation Risk Assessment Modeling System* (BRAMS) software [11]. The *Bioaccumulation Evaluation Screening Tool* (BEST) is one of the two models available in BRAMS software. It has a number of strengths: it is easy to use, requires few parameters, and it is flexible to modify the food chain structure and exposure scenarios. However, BRAMS tool is site-specific, and only one site at a time can be studied. Moreover, results are given in portable document format (PDF). This considerably hinders and slows further analyses of results. Particularly, it is not possible to use digital spatial datasets, map results, or incorporate other spatially arrayed aspects or data to the study. Combining the strengths of the original BEST tool with the numerous capabilities of GIS, a Python code with an interface in ArcMap® (by Environmental Systems Research Institute, Inc. (ESRI®)) is developed in this work, in order to perform spatially distributed bioaccumulation risk analyses. This new tool is based on the framework of BEST model, and hence, it is named Arc-BEST. Arc-BEST predicts concentration of concern contaminants in predators tissues from concentrations in organisms at the bottom of the food chain, which are typically invertebrates. It also estimates carcinogenic and non-carcinogenic risks for humans that consume those species.

Regarding the second objective, the Laurentian Great Lakes are one of the largest fresh surface water system in the planet, covering more than 94,000 square miles and draining more than twice as much land [12]. They support a wealth of biological diversity and unique ecosystems. The Great Lakes have abundant fish stocks harvested by recreational anglers and commercial fisheries. Historically, more than 160 local native communities have incorporated considerable amounts of fish in their diets [13]. However, persistent bioaccumulative toxic chemicals have affected water quality, contaminated fish, and have impacts in the entire ecosystem. PCBs are among these critical contaminants in the Great Lakes [14, 15]. In this work, a screening-level bioaccumulation risk analysis of long-term effects of PCBs is performed, based on concentrations in zebra mussels (*Dreissena polymorpha*), which are invertebrates at the bottom of the food chain. They are an invasive species of the Great

Lakes [16], which have a great filtration capacity and high bioconcentration rates [17], increasing the bioavailability of contaminants for predator species. PCBs concentrations in different-level predators: round goby (*Neogobius melanostomus*) and smallmouth bass (*Micropterus dolomieu*) are predicted. Furthermore, health risks for humans that consume sport fish are estimated for different exposure scenarios. The distribution of the risks in the different lakes is analyzed, and hot spots are identified.

1.3 Importance to Civil and Environmental Engineering

As highlighted above, bioaccumulation of persistent, toxic substances represent a potential hazard for organisms in all compartments of the food web, but particularly to higher-order predators, because the concentration of toxic chemicals can be magnified as the trophic-level increases. It is critical to estimate bioaccumulation in order to predict potentially adverse effects on ecosystems and human health. Knowing the magnitude of these effects can guide the implementation of protective, preventive, and restorative measures, and in general it can help decision-making and the development of sound public policy. To be more specific, a clear example is the elaboration of safe fishing guides and update of fish consumption advisories, which currently exist for some fish in all of the Great Lakes [13]. Other potential applications where bioaccumulation could play an important role are the regulation of wastewater discharges, of dredge material, and the use of toxic chemicals such as pesticides. In short, the integrated management of watersheds, including the evaluation, modeling, and monitoring of water quality, regulation and control of discharges and contaminant loads, and regulation of the different uses of water resources, are areas of civil and environmental engineering where the tool and approach proposed in this work can make a contribution.

1.4 Contributions

The main contributions of Arc-BEST are the following: it enables the automated use of digital spatial data sets, its code is open source, and it can be use in an screening-level risk assessment process. Firstly, the automated use of digital spatial datasets can improve model creation speed, as well as facilitate the analysis, comparison and visualization of results. Furthermore, the model was improved to consider up to four trophic-levels, instead of only three as in the original BEST model. Secondly, Arc-BEST is open-source, so the user can know how the model works, which equations are being used, and modify the code to incorporate additional capabilities. The Python code can also be used as a stand-alone model called by other software. Finally, the USACE and USEPA BEST model was originally developed to help with dredged material management. In this work Arc-BEST is proposed to be used as part of a screening-level risk assessment process, in order to identify hot spots where further studies and monitoring should be performed to ensure humans and ecosystems health. The tool is successfully applied to a case study of PCBs in the Laurentian Great Lakes. Arc-BEST could be of interest for federal, state and other organizations that promote safe practices and that are committed with the protection of the environment; for regulatory agencies and decision makers; and for scientist and researchers.

1.5 Organization of the Thesis

The chapters in this thesis are organized as follows:

- A review of the model is included in Chapter 2. It begins with the description of the background of BEST model, and continues with the methods used to estimate risks due to bioaccumulation of contaminants through the trophic chain.

- Chapter 3 details the implementation of the methodology presented in Chapter 2, including the geoproccessing application created in ArcGIS®.

- Chapter 4 comprises the case study of PCBs in the Great Lakes region. The approach, which is a screening-level risk assessment, is firstly detailed. Based on this approach, the motivation and relevance of the case study are addressed. Finally, the results are presented.

- Chapter 5 discusses the results, including the uncertainties and limitations of the case study. In addition, strengths and limitations of Arc-BEST are included.

- Chapter 6 finishes with the conclusions and findings of the research, and potential future applications of the tool.

CHAPTER 2

MODEL REVIEW

Arc-BEST is based on the framework of the *Bioaccumulation Evaluation Screening Tool* (BEST), released by USACE and USEPA as part of the *Bioaccumulation Risk Assessment Modeling System* (BRAMS) in 2012 [11]. In this work the capability of the model was expanded to consider up to four trophic levels, while the original model only manages three levels. This chapter begins with a background of the original software. Next, it outlines the equations used: 1) to estimate bioaccumulation of contaminants from organisms in one level to predators in the following level, which are based on *biomagnification factors* ($BMFs$); and 2) to calculate human health risks due to consumption of contaminated species, using *cancer slope factor* (CSF) for carcinogenic risks and *reference dose* (RfD) for health risks other than carcinogenic.

2.1 Background

BRAMS is a stand-alone tool for calculating the potential human health and ecological risks associated with bioaccumulation of contaminants. It was released in 2012 by USACE and USEPA [11]. It includes two fully customizable models, *Trophic Trace* (TT) and the *Bioaccumulation Evaluation Screening Tool* (BEST), based on the 2005 USACE *TrophicTrace* and the 1999 EPA Region 1 *bioaccumulation risk assessment model* frameworks, respectively [18]. Arc-BEST, as it names suggests, is based on the approach and equations of BEST.

The model was originally conceived to help with dredged material management, since sediment-associated contaminants, partially due to bioaccumulation and biomagnification in aquatic food chains, are the primary source of environmental risk associated with dredged sediment disposal. Required by the Marine Protection Research and Sanctuaries Act, the current approach (tiered approach) for evaluating dredged materials is outlined in the *Ocean*

Testing Manual and *Inland Testing Manuals* (OTM [19], ITM [20]). The OTM provides a general protocol for evaluating sediment toxicity and determining the suitability of dredged materials for open-water disposal. USEPA and USACE share the responsibility for regulation of this dredged material. This material is potentially unacceptable if animals exposed to it bioaccumulate statistically greater amounts of contaminants than those exposed to reference sediments or higher concentrations than Food and Drugs Administration (FDA) action levels. BEST model can be used in Tier III of OTM and ITM, using data collected during regulatory evaluations of dredged material [18]. Therefore, BEST was originally conceived to estimate bioaccumulation due to trophic transfer and risks associated with contaminants in dredged sediments. The model components are: contaminants concentrations in invertebrate tissues; site food web; receptor exposure scenarios; and contaminant transfer and toxicity factors.

2.2 Methods

In this work a Python code was developed based on BEST models governing equations, following BRAMS Manual [18]. With the script, a geo-processing tool was created: Arc-BEST. This makes the use of digital spatial datasets possible. The model equations are described below.

The original BEST model considers a three level food chain: invertebrates[1], predators, and humans. In Arc-BEST, an extra trophic level is incorporated, which allows the user to create a more realistic and complex scenario. The components of the food chain in Arc-BEST are: invertebrates, first-level predators, second-level predators, and humans. The tool predicts edible tissue concentrations of contaminants in predators species by applying a trophic transfer model to the measured concentrations in prey species. This approach assumes that the prey species represent the diet species typically consumed by predators [18]. The result of edible tissue concentration is used to determine the dose to humans that consume them. The lifetime average daily dose ($LADD$) is calculated for carcinogenic and non-carcinogenic risks.

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[1] BEST model uses invertebrates to represent organisms at the bottom of the trophic chain, mainly because invertebrate species are typically used in bioaccumulation testings. In this work, the use of any species in the first level of the food chain is restrained. However, for convenience the terminology “invertebrates” is used to refer to them.

The model predicts the chemical concentrations in any predator species by applying a trophic transfer model to the measured contaminant concentrations in the corresponding prey species using equation (2.1).

$$C_{Pred} = \frac{C_{Prey}}{NF} \times BMF \times \frac{Lipid_{Pred}}{Lipid_{Prey}} \tag{2.1}$$

where C_{Pred} is the concentration of contaminant in edible tissue of the predator species (in mg/kg), $Lipid_{Pred}$ is the predator's mean lipid fraction (in g lipid/g tissue), $Lipid_{Prey}$ is the prey's mean lipid fraction (in g lipid/g tissue), BMF is the *biomagnification factor* (dimensionless), and C_{Prey} is the concentration of contaminant in edible tissue of the prey species. C_{Prey} must be in μg/g for metals and in ng/g for organic contaminants. NF is the unit normalization factor, which is equal to 1 for metals and equal to 1000 for organic contaminants, to convert from ng/g to μg/g.

The model allows multiplying C_{Prey} by a steady state correction factor ($SSCF$, dimensionless) if the data is obtained from laboratory tests. The $SSCF$ is applied to further estimate prey tissue concentrations under natural exposure periods that are longer than the standard testing duration.

The *biomagnification factor* BMF accounts for accumulation of chemicals in predator's tissue from consumption of preys. Chemicals that biomagnify, or increase their concentration up the food chain, will have $BMFs > 1$ while those that do no biomagnify will have $BMFs \leq 1$.

The result from equation (2.1) is used to determine the dose to humans that consume these species. The lifetime average daily dose ($LADD$, in mg/kg-day) is calculated as follows:

$$LADD = \frac{C_{Pred} \times FI \times F \times IR \times ED}{BW \times LT} \tag{2.2}$$

where C_{Pred} is the edible tissue concentration of humans' diet species (in mg/kg), FI is the fraction ingested (unitless), F is the frequency of ingestion (in days/year), IR is the ingestion rate (in kg/day), ED is the exposure duration (in years), BW is the body weight (in kg), and LT is the lifetime (in days).

To determine the carcinogenic risk level, the $LADD$ is multiplied by an oral *cancer slope* *factor* (CSF) according to equation (2.3). According to USEPA [21]:

> *"Traditionally all cancer effects were considered to lack a threshold, based on the thinking that some risk is associated with all levels of exposure between a dose of zero and the lowest observed tumor response, and that the risk increases in a linear fashion defined by the slope of the line. The slope of the line is termed the Cancer Slope Factor (CSF). The linear approach is used for direct-acting carcinogenic agents, those that cause chemical changes (mutations) in DNA. It is also the default choice for carcinogens when there are insufficient data to demonstrate that the mode of action of the chemical is nonlinear."*

$$Cancer\ Risk = LADD \times CSF \tag{2.3}$$

To determine the non-carcinogenic hazard or hazard index, the $LADD$ is divided by an oral *reference dose* (RfD, in mg/kg-day) according to equation (2.4). According to USEPA [22]:

> *"The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. Usually, doses less than the RfD are not likely to be associated with adverse health risks, and are therefore less likely to be of regulatory concern."*

$$Hazard\,Index = \frac{LADD}{RfD} \tag{2.4}$$

A hazard index greater than 1 is considered indicative of potential health effects. For cancer risks, an acceptable risk upper bound between 1×10^{-4} and 1×10^{-6} is typically applied [18].

Besides calculating cancer and non-cancer risks and comparing them with indicative thresholds, the model also compares C_{Pred} values with FDA (Food and Drug Administration) action levels [23] and with ecological effect levels when available.

CHAPTER 3

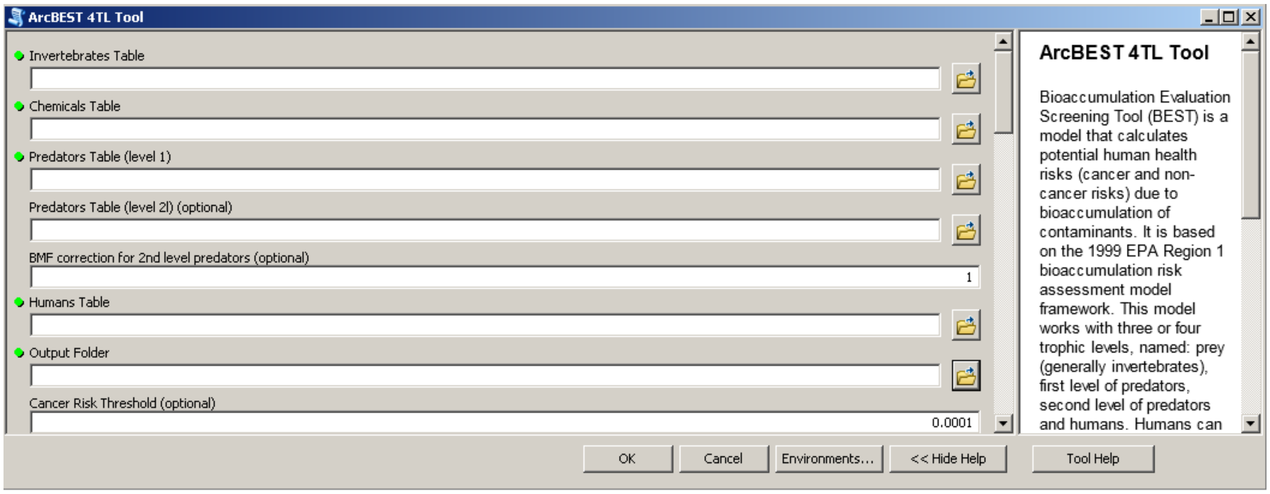
IMPLEMENTATION

Arc-BEST is able to perform the equations presented in Section 2.2 for several locations at the same time. The locations are usually associated with the places where invertebrate (prey) samples are collected. The interface of the tool in Arc-Map® is presented in Figure 3.1.

Arc-BEST has five required inputs: four data tables with information related to invertebrates (preys), chemicals, first-level predators, and humans; and the output folder where the results are saved. It is important to highlight that the input tables can contain multiple chemicals, multiple invertebrate and predator species, and multiple human exposure scenarios. In addition, a data table with information regarding second-order predators is optional, giving the user the possibility to simulate three- and four-level trophic chains. The minimum information (fields) that each tabular dataset must contain is described in Tables 3.1 to 3.4 for invertebrates, chemicals, predators, and humans, respectively. However, it is possible to have additional information. The fields names in each tabular dataset are optional inputs. If the user does not specify them, the default names are used, and if they do not match with the names in the input tables, an error occurs. Other optional inputs are the cancer and non-cancer risk thresholds, the default values are set equal to 1×10^{-4} for cancer risk and 1 for hazard index [11]. Finally, a correction for the BMF between the first- and second-level predators is also an optional input. The BMF specified in the chemicals table (Table 3.2) is the biomagnification factor between invertebrate and first-level predator species. If the user specifies a correction factor as an input, the value from Table 3.2 is multiplied by this factor when estimating the contaminant concentration in second-level predators from first-level predators. Otherwise, a value of 1 (no correction) is used as default. Note that the correction is not used when second-order predators are not considered (e.g. three-level food chain: invertebrates-predators-humans). It is also worth noticing that the $BMFs$ are treated by the tool as chemical- and trophic level-specific, but not species-specific, i.e., the same value is used to calculate the biomagnification of a certain contaminant from one trophic level to the next one.

The outputs are two (when only first-level predators are considered) or three (when both first- and second-order predators are considered) data tables, which are located in the specified output folder. The first table, called "inv_pred.dbf", has, among other parameters, the concentration of contaminant in edible tissue of invertebrate species, and the calculated concentration of contaminant in edible tissue of first-level predator species. An example of this output for the case study analyzed in this thesis is presented in Figure 3.2. The second output table is named "inv_pred_pred2.dbf" (see Figure 3.3), and it contains the comparison between the concentration of contaminant in edible tissue of first- and second-level predator species with FDA action levels and with ecological effect levels through a Boolean expression: 0 if it does not exceed the levels and 1 if it does. If second-order predators are not considered in the study, these comparisons are included in the first table, "inv_pred.dbf". Finally, the third output table, named "inv_pred_hum.dbf" contains the estimated $LADD$ for humans, based on the calculated chemical concentrations in their diet species. It also has the associated cancer risk and hazard index, and the comparison between the risks and their respective thresholds through a Boolean expression. An example of this output is shown in Figure 3.4. The information in each row of each output table is associated to a specific location, defined as "SpecificLoc" (see Table 3.1), where invertebrate's data was collected. Hence, the tables can be easily converted to shapefiles or feature classes based on the latitude and longitude coordinates of the sites. Next, the user can map the results and apply any of the geoprocessing tools available in ArcMap® to analyze them.

Usage instructions of the tool are presented in Appendix A, where a more detailed description of how Arc-BEST manages the relationships between multiple contaminants, invertebrates, predators, and human exposure scenarios is also included.



BMF correction for 2nd level predators (optional): 1

Cancer Risk Threshold (optional): 0.0001

ArcBEST 4TL Tool

Bioaccumulation Evaluation Screening Tool (BEST) is a model that calculates potential human health risks (cancer and non-cancer risks) due to bioaccumulation of contaminants. It is based on the 1999 EPA Region 1 bioaccumulation risk assessment model framework. This model works with three or four trophic levels, named: prey (generally invertebrates), first level of predators, second level of predators and humans. Humans can

Figure 3.1: Arc-BEST tool interface in ArcMap®.

Table 3.1: Minimum fields that the data table for invertebrates (preys) must contain.

Default field name	**Description**
SpecifLoc	Specific location where the sample was taken. It must be a unique identifier of the location.
DataYear	Year when the invertebrate sample were collected.
I$_{N}ame$	Name of the invertebrate species.
Chemical	Chemical name whose concentration was measured in the invertebrates tissues.
Cprey	Chemical concentration in the invertebrates tissues, in μg/g for metals and ng/g for organic contaminants.
I$_{l}ipid$	Lipid content of the invertebrate, in g lipid/g tissue.

Table 3.2: Minimum fields that the data table for contaminants must contain.

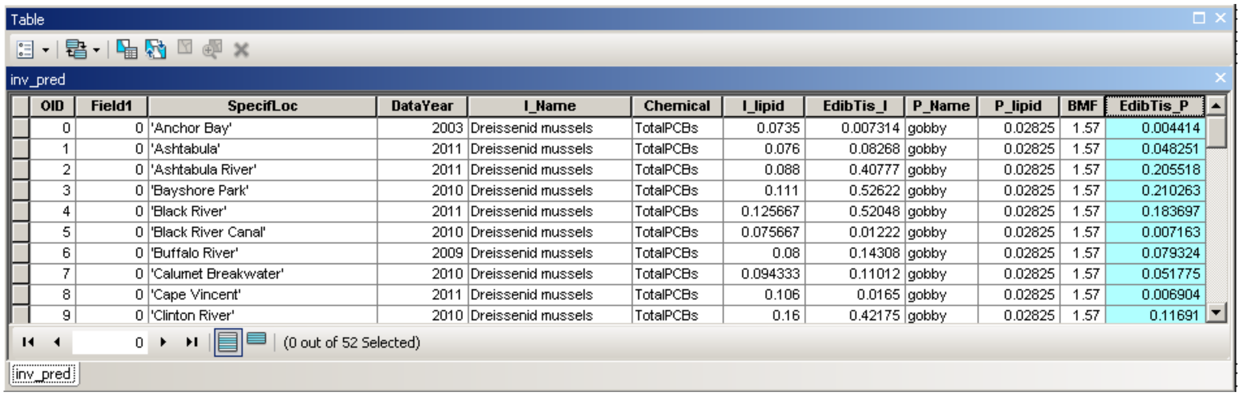
Default field name	**Description**
Chemical	Chemical name. It must match with the name used in the table for invertebrates.
Type	Chemical type: Organic or Metal.
CSF	Oral cancer slope factor, in $(mg/kg - day)^{-1}$.
RfD	Oral reference dose, in $mg/kg - day$.
BMF	Biomagnification factor between invertebrate and first-level predator species.
TEF	Human toxicity equivalent factor. Only for compounds whose toxicity information are uncertain or unavailable.
TEFrel	TEF relation: name of the TEF reference chemical that is going to be used to estimate risks based on TEF value. Only for compounds whose toxicity information are uncertain or unavailable.
SSCF	Steady state correction factor. Only when invertebrate inputs are based on bioaccumulation tests.
FDA$_{A}L$	Food and Drug Administration (FDA) action levels, in ppm.
Eco$_{E}L$	Ecological effect levels, in ppm.

Table 3.3: Minimum fields that the data table for predators (first- and second-level) must contain.

Default field name	**Description**
$\mathrm{P}_{N}ame$	Name of the predator.
$\mathrm{P}_{l}ipid$	Content of lipid, in g lipid/g tissue.
Prey	Name of invertebrate that the predator usually consumes. It must match with the name used in the invertebrates table.

Table 3.4: Minimum fields that the data table for humans must contain.

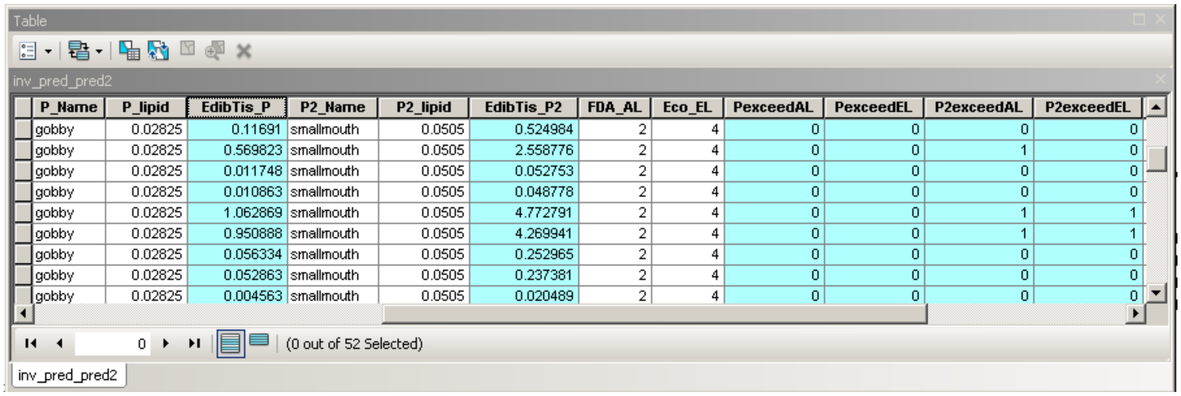
Default field name	**Description**
$\mathrm{H}_{N}ame$	Name to identify human groups with common characteristics, for instance: Weekly consumer.
BodyW	Body weight, in kg.
Lifetime	Lifetime in days.
Diet	Name of species that the humans consume. It must match with the name used in predators table.
Fraction	Fraction ingested.
Freq	Frequency of ingestion, in days/year.
Rate	Ingestion rate, in kg/day.
ExposureT	Exposure time (in years).



OID	Field1	SpecifLoc	DataYear	I_Name	Chemical	I_lipid	EdibTis_I	P_Name	P_lipid	BMF	EdibTis_P
0	0	'Anchor Bay'	2003	Dreissenid mussels	TotalPCBs	0.0735	0.007314	gobby	0.02825	1.57	0.004414
1	0	'Ashtabula'	2011	Dreissenid mussels	TotalPCBs	0.076	0.08268	gobby	0.02825	1.57	0.048251
2	0	'Ashtabula River'	2011	Dreissenid mussels	TotalPCBs	0.088	0.40777	gobby	0.02825	1.57	0.205518
3	0	'Bayshore Park'	2010	Dreissenid mussels	TotalPCBs	0.111	0.52622	gobby	0.02825	1.57	0.210263
4	0	'Black River'	2011	Dreissenid mussels	TotalPCBs	0.125667	0.52048	gobby	0.02825	1.57	0.183697
5	0	'Black River Canal'	2010	Dreissenid mussels	TotalPCBs	0.075667	0.01222	gobby	0.02825	1.57	0.007163
6	0	'Buffalo River'	2009	Dreissenid mussels	TotalPCBs	0.08	0.14308	gobby	0.02825	1.57	0.079324
7	0	'Calumet Breakwater'	2010	Dreissenid mussels	TotalPCBs	0.094333	0.11012	gobby	0.02825	1.57	0.051775
8	0	'Cape Vincent'	2011	Dreissenid mussels	TotalPCBs	0.106	0.0165	gobby	0.02825	1.57	0.006904
9	0	'Clinton River'	2010	Dreissenid mussels	TotalPCBs	0.16	0.42175	gobby	0.02825	1.57	0.11691

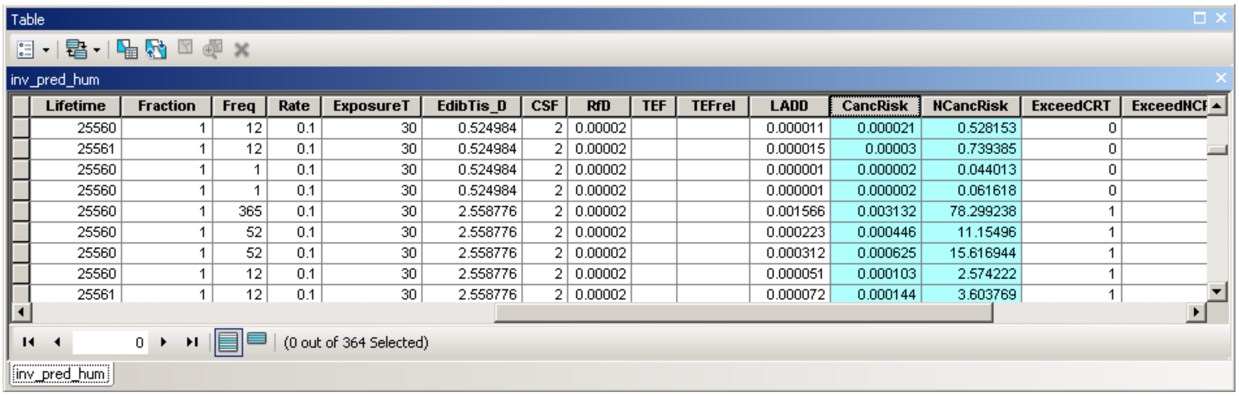
(0 out of 52 Selected)

Figure 3.2: Example of the "inv_pred.dbf" output table, which has the following fields: object id ("OID"), unique identifier of the location ("SpecifLoc"), year when the invertebrate samples were collected ("DataYear"), name of the invertebrate ("I_Name"), name of the contaminant ("Chemical"), lipid content of the invertebrate ("I_lipid"), contaminant concentration in edible tissue of invertebrate ("EdibTis_I"), name of the predator ("P_Name"), lipid content of the predator ("P_lipid"), biomagnification factor ("BMF"), and contaminant concentration in edible tissue of predator ("EdibTis_P", highlighted column).



P_Name	P_lipid	EdibTis_P	P2_Name	P2_lipid	EdibTis_P2	FDA_AL	Eco_EL	PexceedAL	PexceedEL	P2exceedAL	P2exceedEL
gobby	0.02825	0.11691	smallmouth	0.0505	0.524984	2	4	0	0	0	0
gobby	0.02825	0.569823	smallmouth	0.0505	2.558776	2	4	0	0	1	0
gobby	0.02825	0.011748	smallmouth	0.0505	0.052753	2	4	0	0	0	0
gobby	0.02825	0.010863	smallmouth	0.0505	0.048778	2	4	0	0	0	0
gobby	0.02825	1.062869	smallmouth	0.0505	4.772791	2	4	0	0	1	1
gobby	0.02825	0.950888	smallmouth	0.0505	4.269941	2	4	0	0	1	1
gobby	0.02825	0.056334	smallmouth	0.0505	0.252965	2	4	0	0	0	0
gobby	0.02825	0.052863	smallmouth	0.0505	0.237381	2	4	0	0	0	0
gobby	0.02825	0.004563	smallmouth	0.0505	0.020489	2	4	0	0	0	0

Figure 3.3: Example of the “inv_pred_pred2.dbf” output table, which has, in addition to the fields described in Figure 3.2 (some of them are not visible in this figure), the name, lipid content, and contaminant concentration in edible tissue of the second-level predator (“P2_Name”, “P2_lipid”, “EdibTis_P2”, respectively). Furthermore, it has FDA action levels for each chemical (“FDA_AL”) and ecological effect levels for each chemical (“Eco_EL”). The last four highlighted fields compare if “EdibTis_P” and “EdibTis_P2” exceed “FDA_AL” (“PexceedAL” and “P2exceedAL”, respectively) and if they exceed “Eco_EL” (“PexceedEL” and “P2exceedEL”, respectively).



Lifetime	Fraction	Freq	Rate	ExposureT	EdibTis_D	CSF	RfD	TEF	TEFrel	LADD	CancRisk	NCancRisk	ExceedCRT	ExceedNC
25560	1	12	0.1	30	0.524984	2	0.00002			0.000011	0.000021	0.528153	0	
25561	1	12	0.1	30	0.524984	2	0.00002			0.000015	0.00003	0.739385	0	
25560	1	1	0.1	30	0.524984	2	0.00002			0.000001	0.000002	0.044013	0	
25560	1	1	0.1	30	0.524984	2	0.00002			0.000001	0.000002	0.061618	0	
25560	1	365	0.1	30	2.558776	2	0.00002			0.001566	0.003132	78.299238	1	
25560	1	52	0.1	30	2.558776	2	0.00002			0.000223	0.000446	11.15496	1	
25560	1	52	0.1	30	2.558776	2	0.00002			0.000312	0.000625	15.616944	1	
25560	1	12	0.1	30	2.558776	2	0.00002			0.000051	0.000103	2.574222	1	
25561	1	12	0.1	30	2.558776	2	0.00002			0.000072	0.000144	3.603769	1	

Figure 3.4: Example of the “inv_pred_hum.dbf” output table, which has, among other parameters already described in Figures 3.2 and 3.3, the lifetime average daily dose for humans (“LADD”) based on the calculated chemical concentrations in their diet species (“EdibTis_D”), the estimated cancer risk (“CancRisk”) and hazard index (referred as “NCancRisk”), and the comparison between them and risk thresholds (“ExceedCRT” and “ExceedNCRT”).

CHAPTER 4

CASE STUDY: POLYCHLORINATED BIPHENYLS IN THE GREAT LAKES REGION

4.1 Approach

In this thesis, Arc-BEST is proposed to be used as a screening-level assessment of the risks associated to the bioaccumulation of contaminants in aquatic ecosystems. The approach described below is used for the analysis of polychlorinated biphenyls (PCBs) in the Great Lakes region, and it could be extrapolated to other case studies.

A risk assessment process evaluates the probability that adverse effects are occurring or might occur in the future because of the presence of contamination, and it typically follows the following steps: i) hazard identification, ii) exposure assessment, iii) effects assessment, and iv) risk characterization [24].

The first step, hazard identification, involves the general site and contaminant characterization. Moreover, the exposure pathway for contaminants, or in other words the links between contaminant sources and receptors, should be defined. For this case study, the hazard identification is presented in Section 4.2. Firstly, a general description of the chemical structure and properties of PCBs is given, including their high persistence in the environment, which makes them a long-term hazard for humans and ecosystems. The manufacture history and sources of PCBs are detailed, focused on the U.S. and specifically on the Great Lakes region. Moreover, their exposure routes and health effects are mentioned. Secondly, available data of total PCBs concentrations in zebra mussels (*Dreissena polymorpha*) tissue in several sites across the Great Lakes is presented. An exploratory analysis of these data is also performed. And finally, the exposure pathway of PCBs from zebra mussels to higher order predators, including humans, is defined.

The second step, which is the exposure assessment, requires to quantify exposure characteristics of human and ecological receptors identified in the previous step. As mentioned in Section 2.2, Arc-BEST can address ecological risks by comparing contaminants concentrations in predator species with ecological thresholds. This is a simplified approach, and the user cannot define specific exposure characteristics for other ecological receptors, such as mammals or birds. For humans, on the other hand, the exposure scenarios can be well defined in the tool. In Section 4.3, exposure characteristics for humans are detailed.

Effects assessment is the third step, where the potential toxicity of contaminants should be addressed. For this case study, a qualitative description of the potential health effects of PCBs is included in hazard identification, as mentioned above. In effects assessment, a more quantitative description is given, focusing on the parameters used by Arc-BEST to estimate health risks and how their values are obtained. The third step is presented in Section 4.4.

The final step is the risk characterization, where information from previous steps is used to calculate dose and risks, and compared them to established thresholds.These are the results obtained using Arc-BEST, which are presented in Section 4.5. Firstly, the estimated concentrations of contaminants in predators tissue is compared with the Food and Drug Administration (FDA) safety levels and with ecological threshold. Secondly, the cancer risk and hazard index (associated with non-cancer effects) for different human exposure scenarios are detailed, comparing them with recommended thresholds.

Due to the limitations of Arc-BEST, and the uncertainties in the case study, which are both detailed in Chapter 5, in this work the tool is used to perform a screening-level risk assessment, as mentioned before. A screening-level risk assessment is generally followed by a more detailed evaluation of the study site(s). It is used to initially identify the hazards generated by the presence of contaminants and possibly rebut the presumption of risk. The assumptions tend to be conservative or protective and the analysis is based on minimal data. From the point of view of evaluation of risk-management strategies, the possible results of a screening-level assessment could be [25]:

- The degree of contamination is small and poses no significant risk.
- The risk is estimated to be relatively great but the extent of contamination is relatively small. In such cases, a particular risk-management strategy could be identified as feasible and cost effective without further refinement of the risk assessment.

- Potential risks cannot be rebutted and the extent of contamination is relatively great. In these cases more thorough studies should be conducted.

The evaluation of risk-management strategies is out of the scope of this work. The aim of the study is to identify the degree of risk posed by PCBs in the Great Lakes region, following a screening-level risk assessment process.

4.2 Hazard Identification

Poly-chlorinated biphenyls (PCBs) are among critical contaminants in the Great Lakes [14, 15]. In this section, firstly, a brief summary of PCBs characteristics is presented. Secondly, available data of PCBs concentration in zebra mussels (*Dreissena polymorpha*) tissue is described, which is obtained from the *Mussel Watch Program* of the National Oceanic and Atmospheric Administration (NOAA). An exploratory analysis of the data is also included. Finally, the trophic chain considered in this study and its importance in the Great Lakes region is detailed.

4.2.1 Properties, Sources and Effects of Polychlorinated Biphenyls

In this subsection, the characteristics and properties of PCBs, their manufacture history in the U.S., probable sources of in the Great Lakes, and their health effects are detailed. The information presented here is mainly based on the book: *A Risk-Management Strategy for PCB-Contaminated Sediments* [25].

What are PCBs?

Poly-chlorinated biphenyls (PCBs) are aromatic compounds. They consist of two hexagons of carbon atoms connected by carbon-carbon bonds, which is called the biphenyl. PCBs have between 1 and 10 chlorine atoms substituting for hydrogen atoms in the biphenyl rings. Depending on the number and position of the chlorine atoms, 209 different chemical structures are possible, which are called congeners [25].

Properties and Sources of PCBs

Among their main properties, PCBs are nonflammable, are miscible with organic compounds, have low reactivity, and have high chemical and thermal stability. These characteristics made them useful in several industrial applications, such as insulating fluids in electrical transformers and capacitors, as well as in hydraulic systems, surface coatings, and flame retardants. They began to be industrialized in 1929, in complex mixtures of up to 50 or 60 congeners. In the U.S. they were produced almost exclusively by Monsanto under the commercial name of Aroclors. Their commercialization was banned in 1979. Between those years, around 700,000 tons of PCBs were produced in the U.S., and almost 90% was used domestically [25].

Also according to [25], although their commercial manufacture is banned and their disposal from existing equipment is usually regulated, there are still several potential sources that release PCBs to the environment, such as: improper disposal of electric equipment and other products manufactured before 1977 and that contain PCBs; leaks from poorly maintained hazardous waste sites; and combustion of PCB-containing materials. The recycling of PCB-contaminated products (e.g. carbonless copy paper, nonmetallic automobile and truck parts, military equipment, plastics, and asphalt-roofing materials) can keep PCBs in circulation for many years [25]. According to the USEPA, between 1998 and 2011, 45,800 tons of PCBs were registered to remain in service in electrical equipment [26].

Once in the environment, PCBs are slow to biodegrade and are generally persistent in all media [25]. Particularly, they are relatively stable in the atmosphere ad therefore, they are subject to atmospheric transportation [27]. In the Great Lakes region, the United States and Canadian governments created the Integrated Atmospheric Deposition Network in 1990 to investigate the deposition of PCBs from the atmosphere, which was attributed as the primarily source of these toxics in the lakes [28]. The East Coast of the U.S. is the most intense area of historical PCB use in the country, and the Upper Hudson River in eastern New York is a probable source of PCBs to Lake Erie [28]. Chicago seems to be a source of atmospheric concentrations of PCBs to Lake Superior and the Chicago area itself, and a possible source to the east coast of Lake Michigan [27, 28]. More recently, [29] studied loadings from different organic contaminants from Toronto to Lake Ontario. They found that atmospheric was the dominant loading pathway for PCBs.

Once in a water body, PCBs tend to partition to the more organic components of the environment, where the highest concentrations are usually found in fine-grained, organically rich sediments [25]. They can also be freely dissolved in water or associated with dissolved organic carbon. The degradation and bioaccumulation of PCBs is congener specific, so the composition of congener mixtures in the environment can be significantly different from that of the original commercial mixtures [25].

Exposure Routes and Health Effects of PCBs

The USEPA defines several exposure routes for humans [30]: food chain exposure, sediment or soil ingestion, dust or aerosol inhalation and inhalation of evaporated congeners, dermal exposure, and ingestion of water-soluble congeners. According to [25], dermal exposure is more common to occupational contact with PCBs. But the primarily means of exposure to both wildlife and humans is through the food chain due to the bioaccumulation an biomagnification characteristics of these chemicals, and this is particularly true in the Great Lakes region [31, 32].

PCBs have found to have neurotoxic effects in exposed animals and cell cultures, they can affect the metabolism of thyroid hormones, and the immune system. Furthermore, they might contribute directly to carcinogenesis [25].

According to the USEPA [33], there is clear evidence that PCBs cause cancer in animals, and they are probable human carcinogens based on animal studies and epidemiological studies with workers exposed to PCBs. Among non-cancer effects, the most serious ones are:

- Immune effects. Based on studies with Rhesus monkeys, which have very similar immune systems than humans, and other animals, have revealed a number of serious effects on the immune system following exposure to PCBs.
- Reproductive effects. Multiple studies with variety of animals, such as Rhesus monkeys, rats, mice, and mink, have shown potentially serious effects on their reproductive

systems. Moreover, decreased birth weight and decrease in gestational age were found in children born to women who worked with PCBs in factories.

- Neurological effects. Studies with monkeys exposed to PCBs have shown significant and persistent deficits in neurological development. Studies in humans suggest similar effects, including learning deficits and changes in activities.
- Endocrine effects. PCBs can affect thyroid hormone levels in animals and humans, which are critical for normal growth and development. PCB exposures have been associated with changes in thyroid hormone levels in infants in studies conducted in the Netherlands and Japan, but additional research will be required to determine the significance of these effects in the human population.

A thorough review of effects of PCBs on development and reproduction of humans and animals can be found at [34].

Limitations to Determine the Hazards of PCBs

According to [25], most of the data on human health effects from exposures to PCBs are based on occupational exposures or consumption of contaminated fish. However, these data might not be easy to obtain and analyze. For instance, epidemiological studies of workers exposed to PCBs have reported increased mortality from cancer, although results have not been consistent across studies.

Due to limitations of the available human data, studies with animals are performed. In these studies, industrial Aroclor mixtures are generally used. However, commercial mixtures can be substantially different from the composition of PCBs found in the environment, particularly in water and sediments, and from those to which humans and high order predators are exposed through the consumption of contaminated fish. The change of PCBs mixtures over time in the environment is due to a combination of effects, such as volatilization, sorption, solubility, dechlorination, and metabolism [25].

As claimed by [25], the toxicity and biological activity of PCBs is congener specific. Therefore, their bioaccumulation capacity and their health effects could be very different. However, additional data are needed to address this. In this study, only total PCBs concentrations were used, which is believed to be a reasonable approach for a screening-level risk assessment that should be performed with minimal data.

4.2.2 PCBs Concentration in Zebra Mussels

Concentration of total PCBs in zebra mussels (*Dreissena polymorpha*) were obtained for 52 locations in the Great Lakes, indicated in Figure 4.1, from the National Status and Trends (NS&T) program of the NCCOS, NOAA (National Center for Coastal Ocean Science, National Oceanic and Atmospheric Administration). NS&T is comprised of three nationwide programs, and one of them is called *Mussel Watch*. Datasets from *Mussel Watch Program* can be downloaded for free at: `http://egisws02.nos.noaa.gov/nsandt/index.html#`, where total PCBs concentrations in zebra mussels are available. The most recent data for each location was selected, which is generally between 2009 and 2011. One location has data from 2008, one from 2006, and one from 2003. The dataset also has lipid content information, which is used in the implementation of Arc-BEST.

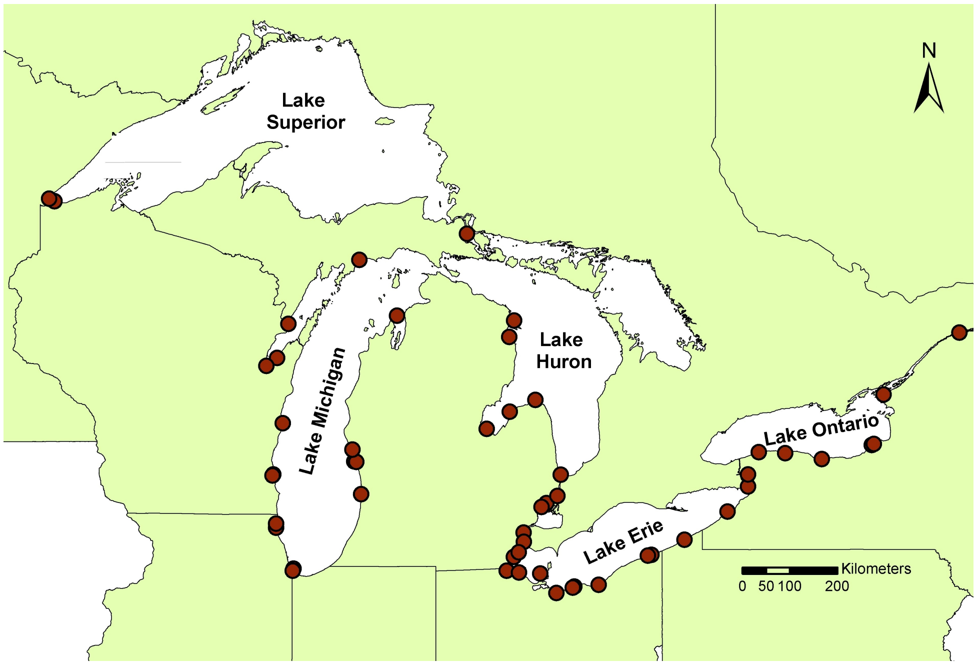


Figure 4.1: Locations in the Great Lakes where concentration of PCBs in zebra mussels were obtained (study sites).

Mussel Watch Program uses a performance based quality assurance process to ensure data quality [35]. Therefore, good quality of the data is assumed. Nevertheless, some exploratory analyses are performed. Particularly, the presence of trends is studied. For most locations, concentrations from 1992-1994 and up to 2009-2011 are available typically every other year. To determine the existence of trends, a Mann-Kendall test [36] is applied to total PCBs concentrations in each of the 52 locations, with a confidence level of 95%. None of the locations present any increasing or decreasing trend. Moreover, with a confidence level of 90%, only two sites are detected to have a decreasing trend, both located in the east coast of Lake Michigan.

However, the Mann-Kendall test detects only monotonic trends [36]; and moreover, the amount of data is limited to preform sound trend analyses (at most 11 years of data are available for a given site). The evolution of PCBs concentrations in zebra mussels tissue are plotted over time for each lake (see Appendix B). In some locations the concentrations remain relatively constant, while in others they oscillate over time, although a regular pattern is not clearly identified visually. A more thorough description of the temporal evolution of PCBs concentrations in zebra mussels tissue can be found in Appendix B, where their correlation with lipid content and with concentration of PCBs in sediments are also presented.

Although PCBs concentrations in zebra mussels do not seem to clearly decline over the last two decades in most of the study sites, there are some recent studies that have found decreasing trends of PCBs in Great Lakes' fish. The work of [37] shows significant declines in PCBs in fillet portions of lake trout and whitefish over the past 20 years, while [38] found decreasing PCBs concentrations in lake trout in the last 34 years, however, the half-lives of these contaminants have increased in later years, and hence, their decline rates have decreased.

As mentioned before, in order to perform the risk analysis in this work, the most recent concentrations of total PCBs in zebra mussels tissue were selected. From the analysis presented in Appendix B, there is no evident justification for selecting any concentration over another. Therefore, the most recent value is assumed to be a reasonable representation of the current concentration in each location.

4.2.3 Exposure Pathway Definition

According to the United States Geological Survey (USGS), zebra mussel (*Dreissena polymorpha*) is one of the two dreissenid mussel species known to have been introduced into the United States, together with quagga mussels (*Dreissena rostriformis bugensis*) [16]. Originally from Eastern Europe, they were picked up in the ballast water of ocean-going ships and brought to the Great Lakes in the 1980s. By 1990 zebra mussels and quagga mussels had infested all of the Great Lakes [39].

The mussels have a high filtering capacity, the tendency to feed on contaminated sediments and algae [40], and high bioconcentration rates [17]. Consequently, contaminants previously destined for sediments can be redistributed into zebra mussels, increasing contaminant bioavailability and the potential transfer of these contaminants to higher levels in the trophic chain [41–43].

Several sport fish that are potential predators of zebra mussels are identified in the Great Lakes. They are: yellow perch and freshwater drum [41], lake whitefish [44], lake sturgeon and catfish [45].

As mentioned before, mussels have a great potential to accumulate contaminants. Moreover, the model assumes that prey species -zebra mussels in this case- are the primary diet species of the next trophic-level predator, which is generally not true for the fish species mentioned in the previous paragraph. This can lead to overestimate the risks if their primary diet species bioaccumulate less amount of chemicals than zebra mussels. On the other hand, the risk could be underestimated when the trophic chain involves more than three levels, as the case of the round goby (*Neogobius melanostomus*) that consumes zebra mussels, and at the same time is a diet species of the smallmouth bass (*Micropterus dolomieu*) [40]. In order to take protective assumptions, which is one of the premises of a screening-level risk assessment, the four-level food chain composed by zebra mussels-round gobies-smallmouth bass-humans is selected for this study.

Round goby is also an invasive species, first detected in the Great Lakes in 1990, and they feed aggressively on zebra mussels [43]. Several piscivorous fish feed on round goby, including commercial and recreational species such as walleye, yellow perch, and smallmouth bass; where the latter seems to be the most important, since field and experimental data suggest that round goby is their preferred prey [43].

4.3 Exposure Assessment

As mentioned in the last section, zebra mussels provide a pathway for contaminants to higher level predators that otherwise could become buried in layers of sediments. A typical aquatic food chain in the Great Lakes is selected for this study: zebra mussel-round goby-smallmouth bass. Shore birds and terrestrial mammals, as well as humans, could be exposed to PCBs through the consumption of any of these species. In this section we attempt to quantify exposure characteristics of human and ecological receptors.

Arc-BEST can address ecological risks by comparing contaminants concentrations in predator species with ecological thresholds. Predator species in this case are round goby and smallmouth bass, whose exposure characteristics are defined by the food chain described in the previous section and by the biomagnification factors, which are detailed in Section 4.4. The comparison with ecological thresholds is a simplified approach, and the user cannot define specific exposure characteristics for other ecological receptors.

On the other hand, the tool allows to define detailed exposure scenarios for humans, which are presented in the following section.

4.3.1 Human Data and Exposure Scenarios

The data required to characterize human exposure scenarios in Arc-BEST are: fraction ingested (dimensionless), frequency (days/year), ingestion rate (kg/day), exposure duration (years), body weight (kg), and lifetime (days).

The fraction ingested is considered equal to 1, so that the information related to fish consumption is only considered in the ingestion rate and in the frequency of ingestion. The ingestion rate is selected as one portion of fish, which is equal to 100 g/day (or 0.1 kg/day, which is approximately 4 oz per day). Rather than selecting a fixed frequency, different scenarios are considered in order to evaluate the health risks based on the ingestion frequency.

These scenarios are presented in Table 4.1.

Table 4.1: Fish ingestion frequency scenarios considered in this study.

Name	**Ingestion frequency [days/year]**
Daily consumer	365
Weekly consumer	52
Monthly consumer	12
Annual consumer	1

The exposure duration of humans to contaminants due to consumption of fish from the Great Lakes is difficult to estimate. As mentioned before, there are no decreasing trends in the concentration of total PCBs in zebra mussels in the last 20 years, so it is not safe to assume that the contamination level will decrease in the future. In order to estimate an average exposure time, data of population mobility in the Midwest was considered. Data of population mobility was obtained from the U.S. Census Bureau (`https://www.census.gov/hhes/migration/data/cps.html`).

For a given year, total and nonmover population was obtained. A person is considered a nonmover if in the previous year he/she lived in the same county than in the year the survey was conducted. If a person moves to another county, state, region or abroad, it is assumed that they are no longer consuming fish from the same site in the Great Lakes. Then, the probability that a person does not move in a given year is estimated as:

$$P(not\ moving\ in\ one\ year) = \frac{Nonmovers}{Total\ Population} \tag{4.1}$$

Thus, the probability that a person does not move in n years is given by:

$$P(not\ moving\ in\ n\ years) = P(not\ moving\ in\ one\ year)^n \tag{4.2}$$

Equation (4.2) is true if the result from equation (4.1) is constant over the years. To estimate the "average" number of years that a person is exposed to contaminated fish from one site, the value of n that gives a probability of non moving equal to 50 % is calculated. The results are presented in Table 4.2, where it can be observed that it is approximately, constant considering data from several years. Rounding up (to be more conservative), a value of 20 years is considered to be the average exposure duration.

Table 4.2: Values of n that give a probability of non moving equal to 50 %, using data of population mobility in the Midwest.

Data year	**n [years]**
2009 to 2010	19
2010 to 2011	17
2011 to 2012	18
2012 to 2013	16
2013 to 2014	18

Lower and upper bounds of 1 and 60 years are also considered in order to estimate error bars for the results.The probability of non moving in 60 years is less than 10 %. Furthermore, 60 years is 75 % of the life expectancy in the U.S., which is equal to 80 years [46]. Hence, 60 years is considered as a reasonable upper exposure limit. The lower bound of 1 year is conservative, since there are people that do not consume any fish (or that do not consume any fish from the Great Lakes).

Regarding body weight, the average weight of an adult person in the U.S. (based on data from 2003 to 2006) is 78.3 kg. Lower and upper bounds are also considered in the estimation of the error bars. The weight of female adults in the 5^{th} percentile is selected as the lower limit, while the weight of male adults in the 95^{th} percentile is considered as the upper bound. These values are equal to 50.5 kg and 122.6 kg, respectively [47].

Finally, lifetime is estimated based on life expectancy at birth in the U.S., which is equal to approximately 80 years (29,200 days), as mentioned above.

4.4 Effects Assessment

A thorough description of the potential health effects of PCBs was presented in Section 4.2, in addition to the limitations of considering total PCBs instead of specific congeners. The former are used in this work, which is consistent with a screening-level risk assessment. In this section, however, the quantification of the effects are discussed, focusing on the parameters used by Arc-BEST.

4.4.1 $BMFs$ and Ecologic Effect Level

Thresholds are used to determine the risks for ecosystems. The estimated PCBs concentration in predator tissues, which in this study are round goby and smallmouth bass, are compared with an ecological effect threshold.

The concentrations in predator tissues are calculated based on *biomagnification factors* ($BMFs$), as detailed in Section 2.2. Kwon *et al* [43] studied the trophic transfer of PCBs in zebra mussel, round goby, and smallmouth bass in four sites in Lake Erie. From their work, which is specific for the species considered in this study and for the Great Lakes, the $BMFs$ between these species are calculated. $BMFs$ are estimated as the rate of lipid normalized PCBs concentrations in each species, and the average between the four sites is used. From mussel to goby, the BMF is equal to 1.57, which is greater than the value of 1.124 recommended by [11] to be used between invertebrates and first-order predators. However, this latter value is not species- or site-specific. Between goby and smallmouth bass, a BMF of 2.53 is obtained. The lipid content for both goby and smallmouth bass are also obtained from [43], while for zebra mussels the lipid content is obtained from *Mussel Watch Program* of the NOAA.

The ecological effects threshold is a contaminant-specific upper bound, but it is not species-specific. For total PCBs, a value of 4 ppm is considered according to [11].

4.4.2 FDA Safety Level, CSF, and RfD

To assess risks for humans the most simple approach is to compare the concentration of PCBs in smallmouth bass, which is the fish consumed by humans, to the Food and Drug Administration (FDA) safety level of 2 ppm [23]. This gives an idea of risk hot spots before considering any exposure scenario. To put this value of 2 ppm under context, it represents "*FDA and EPA levels relating to safety attributes of fish and fishery products published in regulations and guidance. In many cases, these levels represent the point at or above which the agency will take legal action to remove products from the market.*" [23].

However, a more detailed characterization of the risks involves the *cancer slope factor* (CSF) for carcinogenic effects and the *reference dose* (RfD) for non-cancer risks, as shown in Section 2.2. The CSF and the RfD are obtained from the EPA Integrated Risk Information System (IRIS) [30].

The RfD is based on commercial mixtures of PCBs: Aroclor 1016, Aroclor 1284, and Aroclor 1254. For the former and the latter, the RfD for oral exposure is estimated as 7×10^{-5} and 2×10^{-5}, respectively. Both have a medium confidence level, with uncertainty factors (already applied to the mentioned values) in the order of a few hundreds. For Aroclor 1284 there is inadequate and insufficient data to derive a RfD for oral exposure. In order to use protective assumptions, a RfD equal to 2×10^{-5} is considered in this study, since the RfD is in the denominator of the equation used to calculate the hazard index.

Total PCBs are classified by the IRIS as probable human carcinogens. For food chain exposure, which is considered as high risk and high persistence, a CSF of 2 is defined based on the upper bound-estimate. Differently from the RfD, the CSF multiplies the lifetime average daily dose in the equation used to calculate cancer risk.

Finally, as mentioned before, human risks estimated based on the CSF and the RfD are also compared to recommended thresholds. For cancer risks, a value of 1×10^{-4} is considered, while for hazard index, which represents non-carcinogenic health effects, a value of 1 is used, both based on [11].

4.5 Risk Characterization

Using the information presented in previous steps, the concentration of total PCBs in round goby and smallmouth bass are calculated and compared to FDA and ecological effect levels. Furthermore, the cancer risk and hazard index are estimated for the different human exposure scenarios, and compared to established thresholds. The considered assumptions are detailed below.

Assumptions

Besides the simplifications and assumptions in the model's equations, the following are the most important assumptions in this study:

- The $BMFs$ estimated from the work of [43] represent the typical trophic transfer of PCBs from zebra mussels to round goby, and from goby to smallmouth bass in all the sites analyzed in this work.
- The most recent concentration of PCBs in zebra mussel tissues from *Mussel Watch Program* of the NOAA are assumed to be a reasonable assumption of current concentration levels.
- All organisms are assumed to feed and remain at each of the sites. This is true for sessile mussels, but it is an assumption for fish species. According to [43], goby are territorial and mobility of smallmouth bass is limited, only 1 to 3 km during multiple-season field studies. All sites are more than 3 km appart.
- Risk ranges presented in Section 4.5.2 only consider uncertainty in human exposure scenarios, as described in Section 4.3.1.

Arc-BEST takes 14.17 seconds to run the case study.

4.5.1 FDA and Ecological Effect Levels

Before evaluating the risks, the simplest analysis that can be done is to compare the estimated concentration of total PCBs in predators tissue with the FDA safety level of 2 ppm and ecological effect level of 4 ppm. These results are presented in Figure 4.2. Figure 4.2a shows the locations where PCBs concentration exceeds these limits in smallmouth bass tissue. The FDA safety level is exceeded in six locations, mainly in the west coast of Lake Michigan, but also in one site in Lake Erie, and in one site in Lake Ontario. These sites are located in relatively high populated areas, usually between 100 and 1,000 people per square mile. Furthermore, three of them are very close to important urban centers (with more than 1,000 people per square mile), such as Chicago (southest location at Lake Michigan), Cleveland (Lake Erie), and Rochester (Lake Ontario).

The magnitude of PCBs concentration in predators tissue is presented in Figure 4.2b. It can be observed that, for round goby, the FDA recommended limit is exceeded in only one location, while the ecological effect level is not exceeded in any site. For smallmouth bass, the FDA bound is exceeded in the six locations mentioned above, and the ecological effect level is exceeded in three of those six sites. In the sites presented in Figure 4.2b, the concentration of PCBs in smallmouth bass tissue is generally between -or slightly above- the considered FDA and ecological levels. However, in "Sheboygan River", the concentration is extremely higher, reaching a value of 17 ppm. It is important to highlight that this site is very close to the city of Sheboygan.

4.5.2 Human Health Risks

In this section the risk for humans that consume contaminated smallmouth bass from the Great Lakes is evaluated. As described in Section 4.3.1 the cancer risk and hazard index are estimated for a person with average body weight, average exposure time based on mobility data, and expected life span of 80 years. Lower and upper bounds for body weight are considered in order to estimate error bars for the results. In addition, different ingestion scenarios are considered: once per day (365 day/year), once per week (52 day/year, once per month (12 day/year), and once per year (1 day/year). This way, risks due to different consumption rates can be compared. The results are presented for each lake: Michigan, Huron, Erie, and Ontario. In Lake Superior there are not enough sites to perform a thorough analysis.

The results are presented in Figures 4.3 to 4.6 for Lakes Michigan, Huron, Erie, and Ontario respectively. Each figure has two panels: in panel a) the study sites are presented in the map of each lake, and a gray-scale is used to indicate the distribution of the risk, where darker colors represent higher human health risks; while in panel b) the average cancer risk level and the hazard index for each site is shown, together with error bars indicating lower and upper bounds. In panel b) the sites are sorted from west to east and from north to south along the coastline. A threshold of 1×10^{-4} is considered for cancer risks, and a threshold of 1 is considered for the hazard index. The cancer risk can be interpreted as the probability of developing cancer during a lifetime due to the consumption of fish that are contaminated with PCBs; if it is lower than 1×10^{-4}, it is considered potentially safe to consume fish (for a given ingestion rate). Note that "potentially safe" is used instead of "safe", given that the presence of other toxic compounds is not studied in this work. This is further analyzed in Chapter 5. The cancer risk threshold can be interpreted as follows: from 10,000 people that consume those fish, one person will likely develop cancer due to ingestion of PCBs that are present in fish tissues. On the other hand, the hazard index represents all adverse health effects other than cancer. As explained in Section 2.2, it is the rate between the $LADD$ and the reference dose. The latter is considered as the maximum dose for which no adverse effects are observed during a lifetime. If the hazard index is greater than one, it means that the $LADD$ is greater than the reference dose, which is not safe.

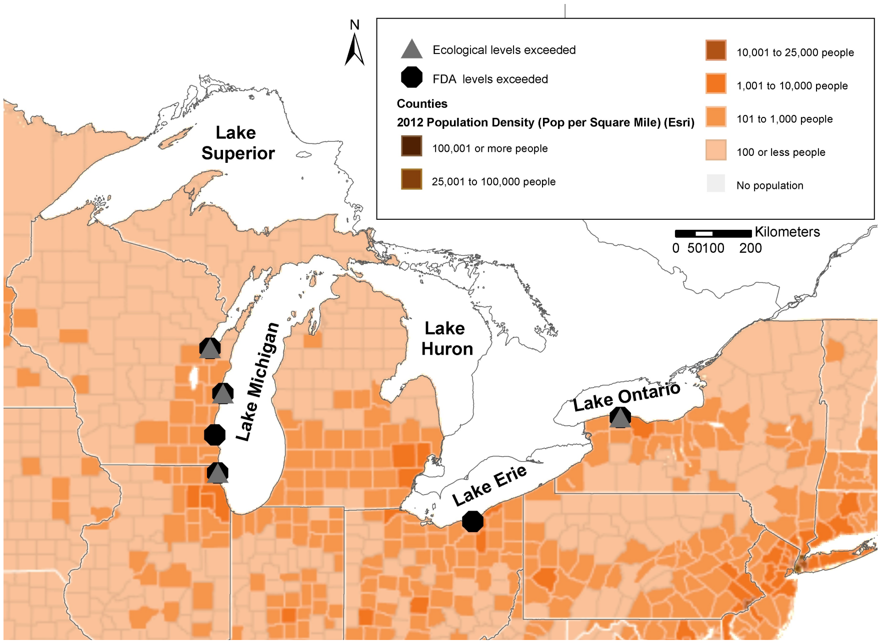
Figure 4.3a shows that higher health risks are estimated in the west coast of Lake Michigan. This can also be observed in Figure 4.3b, where the same sites are sorted from west to east and from north to south. Considering the thresholds mentioned above, overall it is potentially safe to consume fish only once per year or less frequently. However, in the sites located at the south and east coasts of the lake, it is potentially safe to consume fish once per month, and even once per week if the average risk values are considered. The site with the highest risk is "Sheboygan River", which is near the city of Sheboygan, a relatively high populated area with 100 to 1,000 people per square mile. Other sites with high risks that are located near important urban centers are "Waukegan Harbor", "Milwaukee Alternate", and "Milwaukee Bay". In this areas the population density is more than 1,000 people per square mile.

According to Figure 4.4a, the sites with the highest risks in Lake Huron are located in Saginaw Bay. Compared with the considered thresholds, it is potentially safe to consume fish once per week or less frequently, except for "Saginaw River", where an ingestion rate of once per month seems to be the safe limit regarding PCBs toxicity (Figure 4.4b). It is important to highlight that this site is located near a relatively high populated area, with 100 to 1,000 people per square mile. Considering the average risk, even an ingestion rate of 365 days/year is potentially safe in the sites of Lake Huron, except for "Saginaw River".

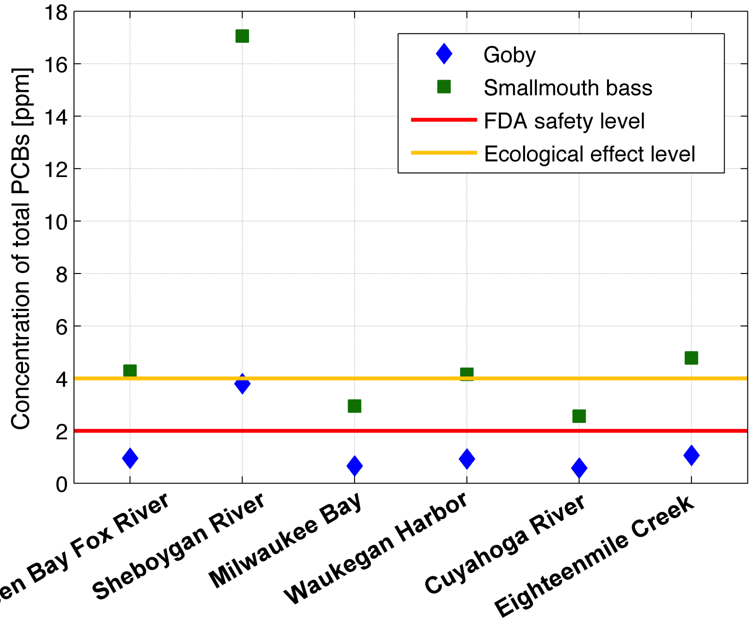
In Lake Erie, it is difficult to identify safer fishing areas from Figure 4.5a due to the amount of sites in this lake. However, from Figure 4.5b it can be observed that the risk fluctuates along the coastline. Overall it is potentially safe to consume fish once per month or less frequently if the average values of risk are considered. Moreover, for almost all the sites the risks exceed their respective thresholds for an ingestion rate of once per year. Regarding population density, the entire coast of this lake is relatively highly populated, with population rates between 100 and 1,000 people per square mile or more. The site with highest risk, "Cuyahoga River", is near the important urban area of Cleveland (south coast of Lake Erie). Other sites with relatively high risks are close to the highly populated areas of Detroit and Toledo (east coast of Lake Erie).

For Lake Ontario, the risk levels do not seem to follow any clear pattern from Figure 4.6a. On the other hand, from Figure 4.6b it can be observed that there is one site with outstanding risk values, which is "Eighteenmile Creek". Here, the risk thresholds are exceeded for a consumption rate of once per month. In all the other sites, a consumption rate of once per week seems to be safe regarding PCBs toxicity. The coast of Lake Ontario is also relatively highly populated, being Rochester the main urban center in the U.S. coast. "Eighteenmile Creek" is not very far from this area.

Overall, from Figures 4.3 to 4.6, it can be observed that the risk levels are in general high compared to the considered thresholds, and non-cancer risks (i.e., hazard indices) seem to be the main hazard. The lake that seems to present the lowest risks is Lake Huron, at least for the sites under study. To consume smallmouth bass once per month seems to be a potentially safe frequency, except for a few sites in Lake Michigan and one site in Lake Ontario. However, as stated in Section 4.1, this is an screening-level risk assessment. Hence, the risks values obtained have a considerable level of uncertainty.

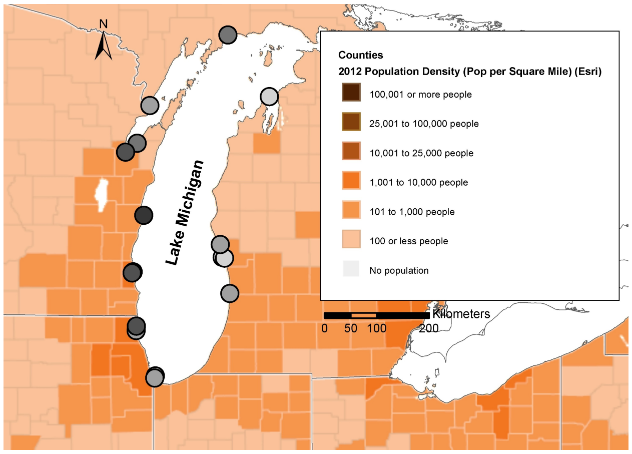


(a) Locations where FDA and ecological levels are exceeded

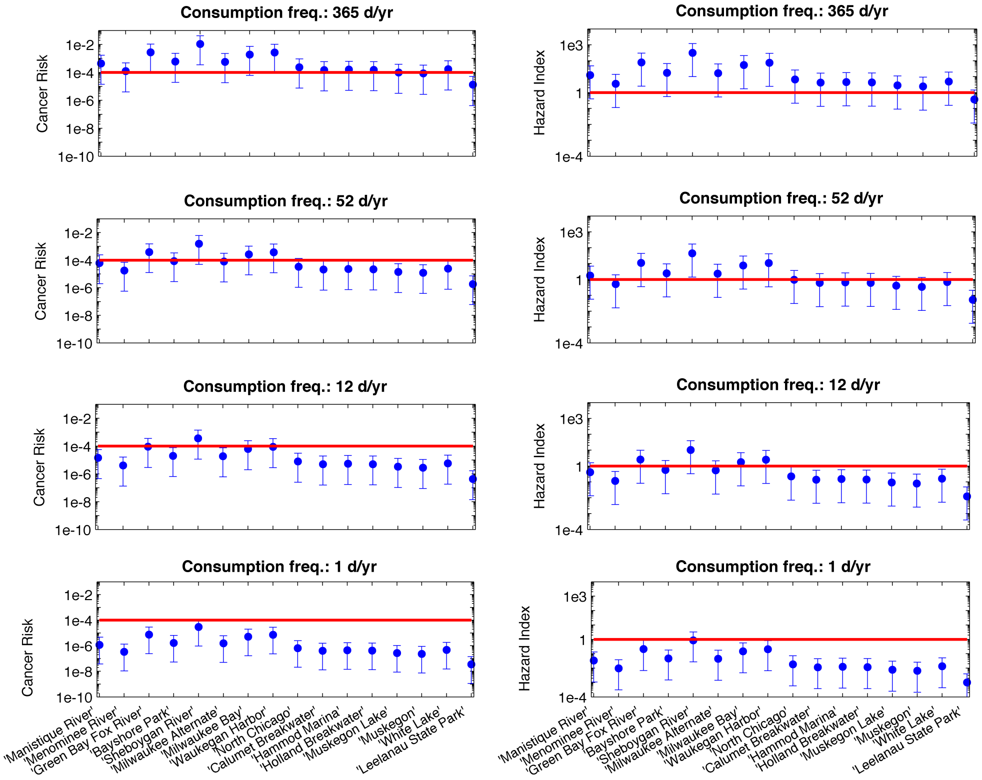


(b) Concentration of total PCBs in predators tissues

Figure 4.2: a) Locations where FDA safety level is exceeded (black dots), and where ecological effect level is exceeded (grey triangles), both in smallmouth bass tissue. U.S. population density in the surroundings of the lakes is also presented. b) Concentration of total PCBs in goby (blue markers) and smallmouth bass (green markers) tissues for the same locations presented in a), which are sorted following the coastline from west to east and north to south. FDA safety level and ecological effect level are also indicated (solid lines).

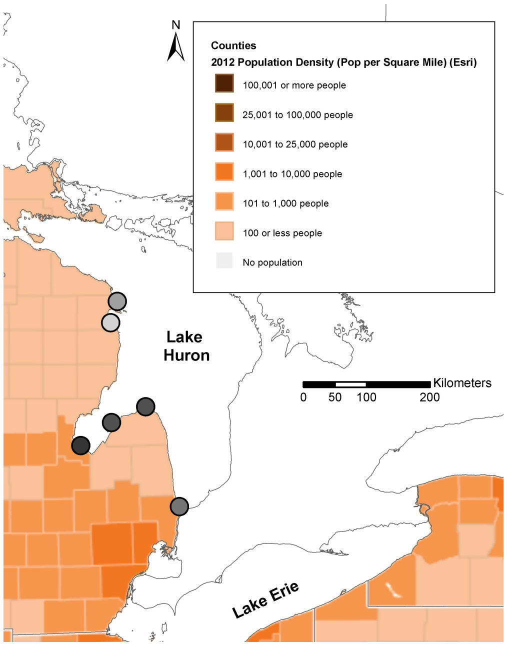


(a) Locations in Lake Michigan

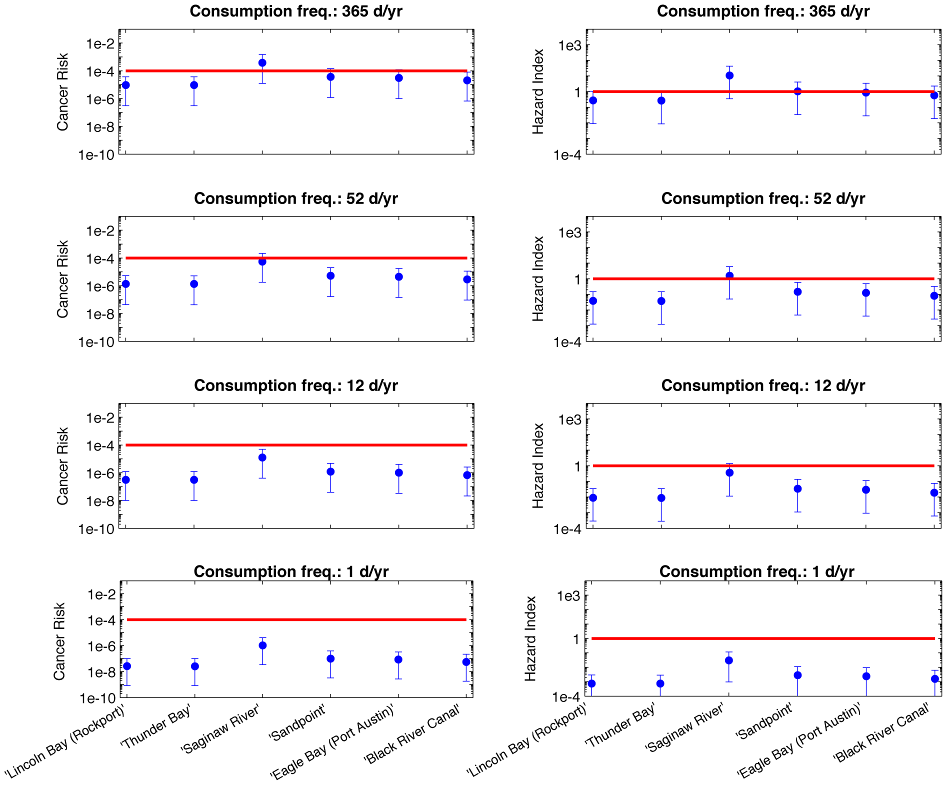


(b) Cancer risk (left) and hazard index (right) based on ingestion rates.

Figure 4.3: a) Study sites in Lake Michigan, where darker colors indicate higher health risks. U.S. population density in the surroundings of the lakes is also presented. b) Average cancer risk (left) and hazard index (right) levels for the same locations presented in a), which are sorted following the coastline from west to east and from north to south. Upper and lower bounds for the risks are presented. Risk thresholds (1×10^{-4} for cancer risk and 1 for the hazard index) are also indicated (solid red lines).

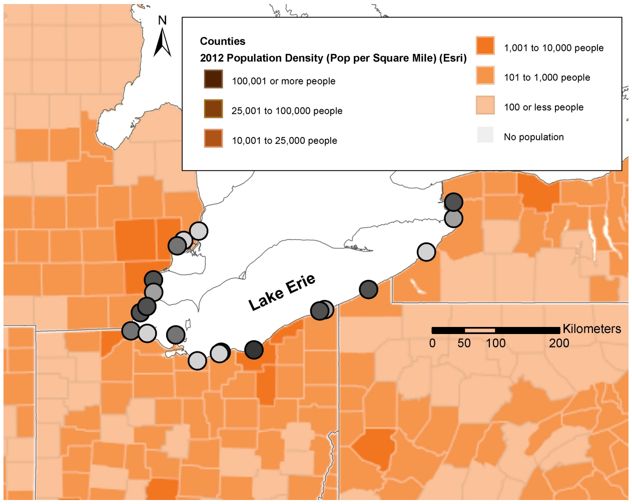


(a) Locations in Lake Huron

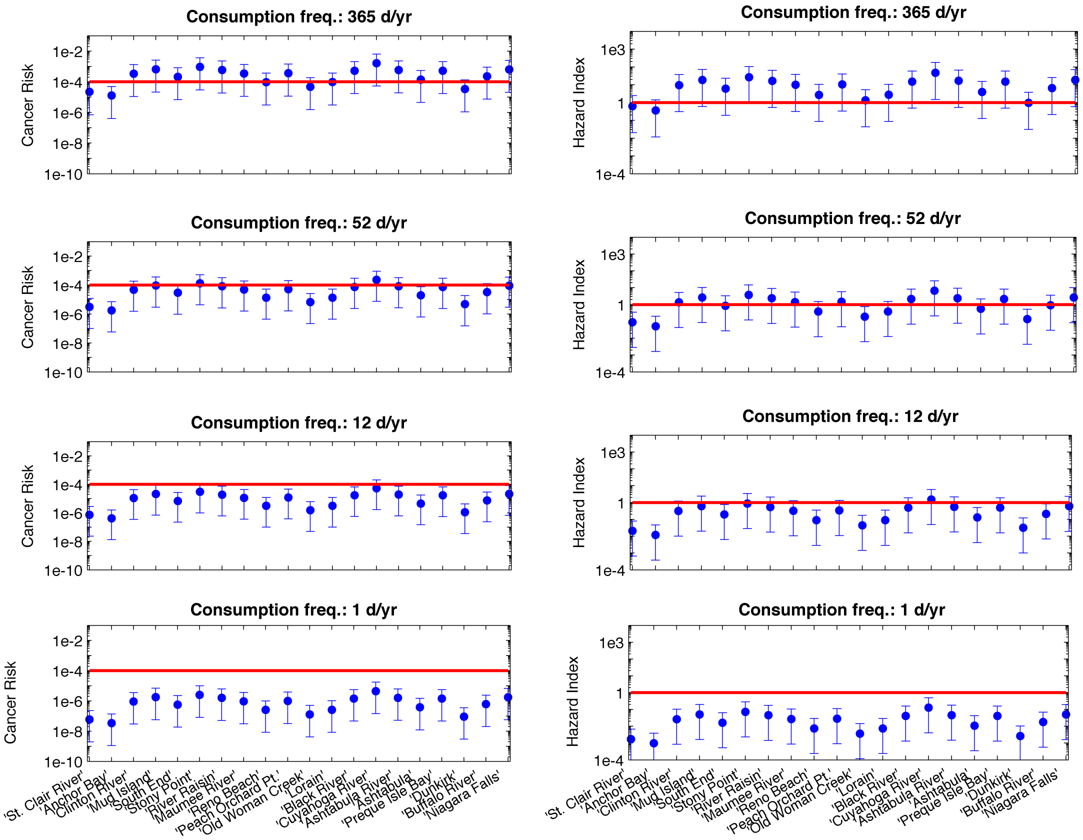


(b) Cancer risk (left) and hazard index (right) based on ingestion rates.

Figure 4.4: Same as Figure 4.3 but for Lake Huron.

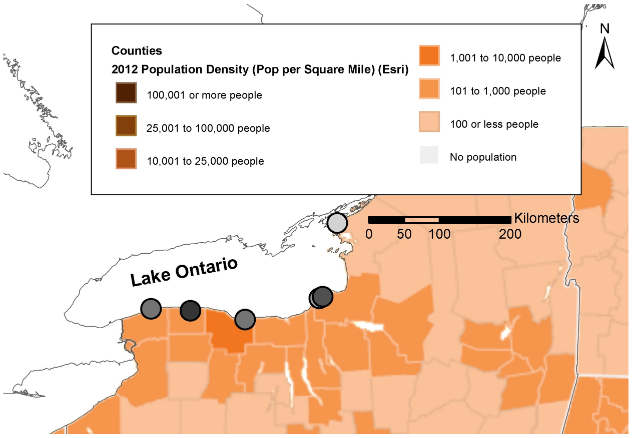


(a) Locations in Lake Erie

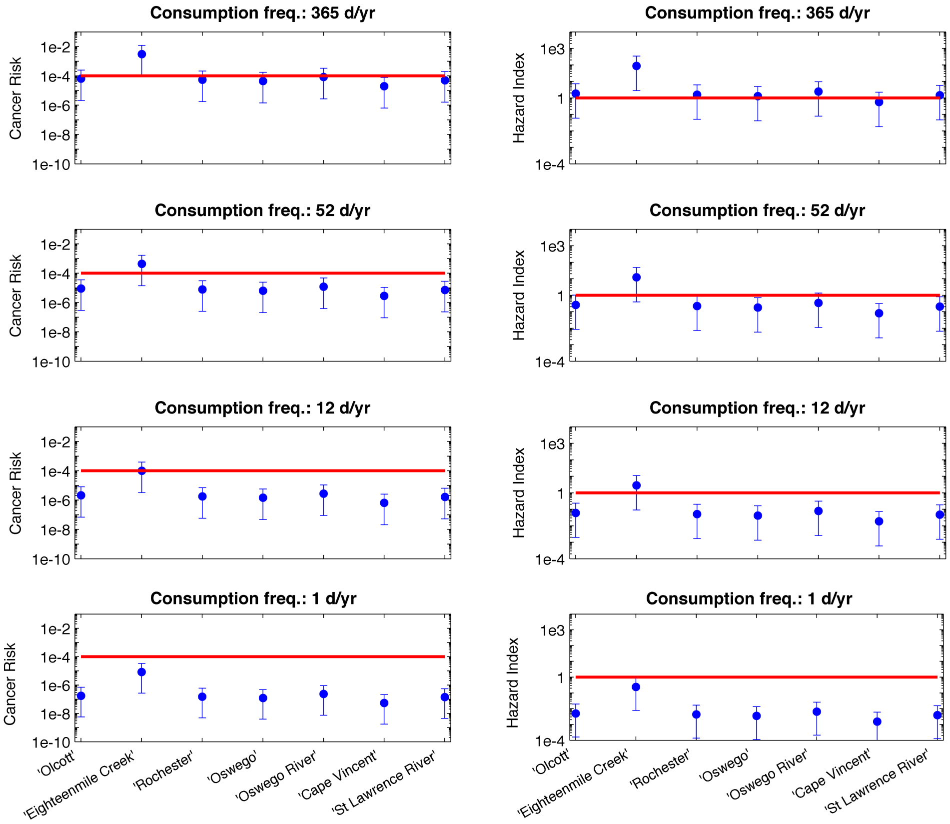


(b) Cancer risk (left) and hazard index (right) based on ingestion rates.

Figure 4.5: Same as Figure 4.3 but for Lake Erie.



(a) Locations in Lake Ontario



(b) Cancer risk (left) and hazard index (right) based on ingestion rates.

Figure 4.6: Same as Figure 4.3 but for Lake Ontario.

CHAPTER 5

DISCUSSION

5.1 Polychlorinated Biphenyls in the Great Lakes Region

Firstly, it is important to highlight that the assumptions and analysis of results are meant to be conservative. As stated in the previous chapter, zebra mussels have a high filtering capacity and the tendency to feed on contaminated sediments and algae, in addition to high biocconcentration rates. This could overestimate the calculated health risks, since other sport fish consumed by humans that primarily feed on other species may bioaccumulate less amount of PCBs than the smallmouth bass. But it is consistent with a conservative analysis, which is the goal in a screening-level risk assessment.

In the next subsectionsthe analysis of the results is presented first, followed by a description of the uncertainties and limitations of the study, and finally a summary with the conclusions regarding the case study.

5.1.1 Analysis of Results

In terms of highest hazard levels, there are six critical sites, where total PCBs concentration in smallmouth bass tissue exceeds the FDA safety level of 2 ppm. Four of them are located in the west coast of Lake Michigan, one in Lake Erie, and one in Lake Ontario. They are all located in areas of relatively high population density, and three of them are very close to important urban centers: Chicago, Cleveland, and Rochester, which are indicated in Figure 5.1. There is one particular location where PCBs concentration is estimated to be considerably higher than in the rest of the sites, which is “Sheboygan River”, shown in blue in Figure 5.1. In this site the concentration is 4 to 8 times higher than in the other five sites.

As indicated in the previous chapter, historical sources of PCBs to the Great Lakes are industrial plants, while current sources could be atmospheric deposition, illegal disposal of PCB-containing products and leaks from hazardous waste sites or old factories. PCBs are highly persistent compounds, and hence, they can be in circulation for many years in the environment, eventually becoming available for bioaccumulation. In the case of Sheboygan River, the main source of PCBs was a former industrial plant that manufactured refrigeration compressors [48].

Sheboygan River was classified as an area of concern (AOC) by the USEPA [49], which encompasses the lower Sheboygan River downstream from the Sheboygan Falls Dam, including the harbor and near-shore waters of Lake Michigan. An AOC is a location that has experienced environmental degradation. The former Tecumseh Product Co. plant in Sheboygan Falls is considered the primary source of PCB contamination in river sediment [48]. The Wisconsin Department of Natural Resources has fishing warnings downstream of the Sheboygan Falls Dam due to the high levels of PCB concentration in fish [50]. With a millionaire budget, dredging of contaminated sediments and habitat restoration projects in Sheboygan AOC began in August 2012, and concluded in June 2013 [49,51]. The data used for this study is from 2011, previous to the beginning of the restoration activities. Although it could take years to see environmental improvements after the clean up [51], the current levels of PCBs concentration could be lower than those estimated in this work.

Regarding human health risks, results for each lake were presented: Michigan, Huron, Erie, and Ontario. Lake Superior was not considered because of lack of data. Furthermore, different fish consumption scenarios were analyzed: daily, weekly, monthly, and annual consumers. Overall, the estimated risks are relatively high, and non-cancer risks (i.e., hazard indices) seem to represent the greatest hazard in the region.

To put the consumption scenarios in terms of real consumption rates, the study *Estimated Per Capita Fish Consumption in the United States* was considered [52]. According to this study, and assuming that the portion of fish fillet in one meal weights 100 grams (approximately 4 oz), the frequency of freshwater fish consumption is about 29 times per year, which is slightly more than twice per month. When the 90^{th} percentile is considered, this number increases to approximately 69 meals per year. Specifically in the Great Lakes states, adults consume on average 38 meals per year [13]. In general, the fish consumed by a person would

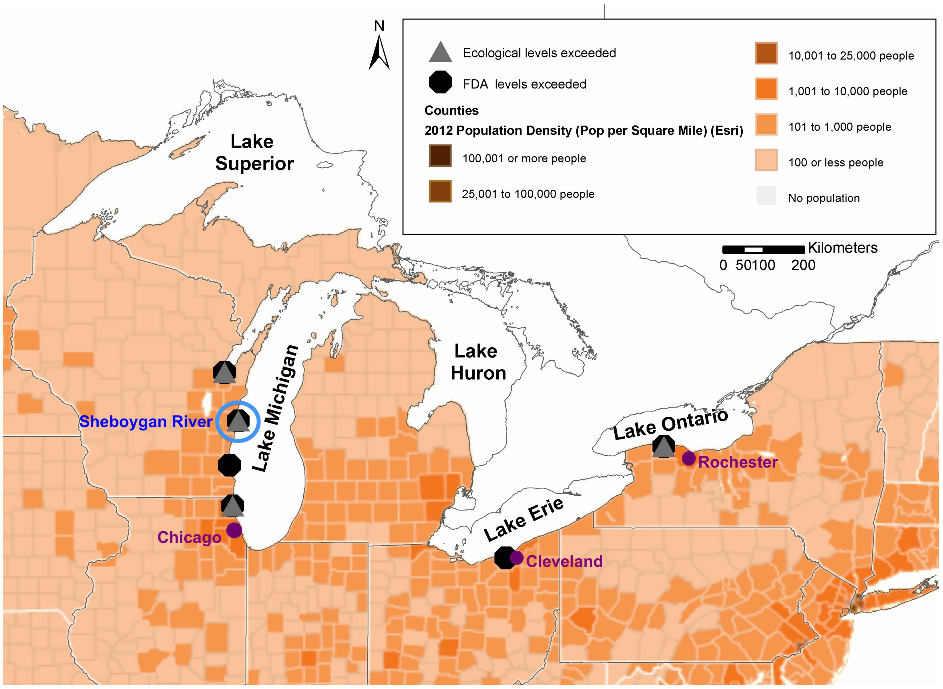
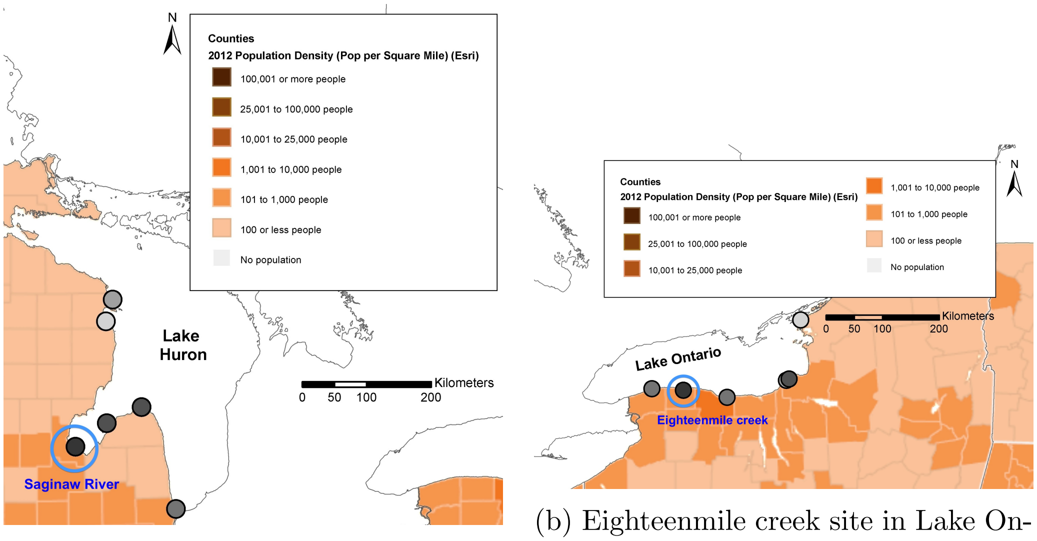


Figure 5.1: Same as Figure 4.2a. Purple dots indicate the locations of highly populated urban centers near sites where FDA safety level for total PCBs concentration in fish tissue is exceeded. The site with highest concentration level, Sheboygan River, is indicated in blue.

likely not come all from the Great Lakes. However, in order to be conservative, the risks for weekly consumers should be analyzed. A daily consumer seems excessively conservative considering the average consumption rate, and even for a consumer in the 90^{th} percentile.

According to the results of the screening-level risk assessment, the health risks due to PCBs for a weekly consumer are relatively small only in Lake Huron and Lake Ontario. However, even in these lakes, there are a couple of isolated sites where the hazard index for a monthly consumer is higher than the considered threshold. They are "Saginaw River" in Lake Huron and "Eighteenmile Creek" in Lake Ontario, both shown in Figure 5.2.

On the other hand, in Lake Michigan and Lake Erie, for a weekly consumer the hazard index is greater than the considered threshold in almost all the sites. The east coast of Lake Michigan seems, however, potentially safe for monthly consumers. Besides this last result, the general conclusion for Lake Michigan and Lake Erie is that the presumption of risks imposed by bioaccumulation of PCBs cannot be rebutted in these lakes. As revealed by the screening-level risk assessment performed in this work, the risk and extent of contamination



(a) Saginaw River site in Lake Huron

(b) Eighteenmile creek site in Lake Ontario

Figure 5.2: Sites with highest risks in a) Lake Huron and b) Lake Ontario. In both cases the hazard index for a monthly consumer exceeds the considered threshold of 1.

are predicted to be relatively great in both lakes.

5.1.2 Uncertainties and Limitations of the Case Study

As in every model, there are sources of uncertainties embedded in the parameters, data, and assumptions of the study, which are discussed in the following paragraphs.

Firstly, Arc-BEST calculates concentration of PCBs in predators tissue using a trophic transfer model based on *biomagnification factors* ($BMFs$). These factors depend primarily on the trophic level of the prey and predator species, as well as the contaminant, but they can vary with the species under study and with environmental conditions. In this work, $BMFs$ that are specific for the species under study and for the Great Lakes are used, which are obtained from the work of [43]. This significantly reduces the uncertainty incorporated by these parameters in the results compared to factors that are general for any physical location and not species-specific, such as the $BMFs$ suggested by [11]. However, another source of uncertainty is the food chain, which in this case consists of: zebra mussels, round goby, smallmouth bass, and humans. As mentioned before, this is a typical food chain in the Great Lakes region, composed by two invasive species -the mussels and the goby- that provide a pathway for contaminants to reach higher level predators. The mussels have a high filtering capacity, the tendency to feed on contaminated sediments and algae [40], and high biocconcentration rates [17]. These factors probably overestimate the health risks, since humans also consume fish species other than smallmouth bass, and in general fish also consume organisms that bioaccumulate less amount of contaminants than mussels. As the tool uses statistical relationships averaged over long periods of time, the results are considered to be conservative using the selected food chain. This follows the spirit of a screening-level risk assessment, where the goal is to make conservative assumptions.

Secondly, the model computes the average daily dose for humans that consume contaminated species. These are referred as the consumption scenarios in this work. As described in the previous chapter, different consumption scenarios are defined: daily, weekly, monthly, and annual. Furthermore, bounds for body weight and exposure duration for humans are considered in order to obtain lower and upper limits for the health risks in each consumption scenario. This way, part of the uncertainty incorporated by the lifetime average daily dose is captured, allowing to make a more confident interpretation of the results. However, because human consumption during long periods of time (up to 60 years) are being analyzed, there is uncertainty associated with the concentration of PCBs in future years. To put it in other words, the tool estimates the risk levels assuming the most updated concentrations of contaminants available, and considering that they remain constant during the exposure period. As previously analyzed in Chapter 4, no increasing or decreasing trends where found in the concentration of PCBs in zebra mussels tissue during the last two decades. Although common sense would suggest that the concentrations should eventually decrease considering the long-term banned production of PCBs, there is no evidence to believe that, nor to believe that they would increase. Therefore, it seems a reasonable assumption to consider constant concentrations.

Thirdly, the tool estimates cancer risk and hazard index using the *cancer slope factor* (CSF) and the *reference dose* (RfD), respectively, both for total PCBs. On the one hand, these parameters have intrinsic uncertainties due to the fact that there are few epidemiological studies with humans, and they are mainly based on laboratory studies with animals. The USEPA affects both parameters by uncertainty factors, which leads to more protective results. On the other hand, the CSF and RfD are based on studies with Aroclors, which are industrial mixtures of PCBs. As mentioned in Chapter 4, different PCB congeners could have different toxicity and biological activity. The uncertainty posed by considering total PCBs instead of specific congeners could not be quantified in this study due to lack of available data. However, this is an acceptable level of uncertainty for a screening-level risk assessment, where minimal data is used.

In the previous paragraphs, uncertainties and limitation that are mainly related with the parameters of the model and assumptions of the modeler were described. Another limitation of the study is data availability. All the analyzed sites are located in the US coast of the lakes, and sometimes they are long distances apart. Hence, the results cannot be extrapolated to every location in the lakes. Between two sites along the shore, interpolation of results seems reasonable if there is not a point source of PCBs between them. Regarding offshore locations, we could think that the risk should diminish since they are far from urban centers that are -or were once- potential sources of PCBs to the water and sediments. But this assumption is not valid a priori, since one of the main sources of PCBs to the Great Lakes could be atmospheric transport, as described before. An assumption that seems more valid is that people tend to fish near the coast rather than far away from it, but yet this is not proved in this work. Overall, the extrapolation of results to any location in the lakes could be reasonable if more densely and uniformly distributed sites were available.

Finally, there is uncertainty related to the presence of other contaminants, which are not analyzed in this work. One could argue that this is out of the scope of the study, where the goal is to analyze the potential health risks due to the presence of PCBs in the Great Lakes region. However, interactions between different contaminants are uncertain, and the hazard generated by several contaminants together could be worse than the sum of each of them acting individually. These interactions are not clear and there is still a lot of research to be done in this area. For the Great Lakes region, a previous risk analysis for heavy metals was performed using Arc-BEST [53]. It was found that the level of risks due to metals do not seem to represent a great hazard for human health, since the thresholds for cancer and non-cancer risks were exceeded in some sites only for a daily consumer during a 30-year exposure duration. In addition, trends for metal concentrations in dresissenid mussels were studied and, in general, it was found that the levels remained constant or had a decreasing trend in the last two decades. Regarding the present study, it is important to clarify that only PCBs are considered, and hence, if the risk is relatively low in one site, we cannot conclude that it is safe to consume fish from that site or that the local ecosystem is not threaten by contaminants.

5.2 Strengths and Limitations of Arc-BEST

Arc-BEST has several strengths that are indicated below. Some of them are inherited from the original BEST model, however, it has some unique contributions and improvements. As any model, it also has limitations, which are described below as well.

In the first place, Arc-BEST is a friendly and easy-to-use tool. As described in Chapter 3, four tabular datasets are needed with information regarding invertebrates, chemicals, predators, and human consumption scenarios. They can be easily imported to ArcGIS® from other softwares, such as Excel. Once the calculations are performed by the tool, the results can be easily converted into a shapefile or feature class based on latitude and longitude information, and after that any geoprocessing tool from ArcGIS® can be applied to visualize and analyze the results.

Secondly, the model needs few parameters and data. The most important data is the concentration of contaminants under study in invertebrate species (or in the species considered at the bottom of the food chain). Also, this is potentially the most time-consuming and costly data to obtain. According to [54], collecting samples and performing bioaccumulation tests could cost about $1000 per sample (in 2002). However, there is free available data, for example from NOAA's *Mussel Watch Program*, which is the longest running estuarine and coastal -including the Great Lakes- pollutant monitoring effort conducted in the United States that is national in scope each year [35]. Apart from these data, the tool requires lipid content for the different species, which is relatively easy to obtain from bibliography if measures are not available, and the exposure scenarios for humans, which should be defined based on the case study. The selection of the food chain also depends on the location and environment under study. Arc-BEST allows the user to consider up to four levels in the food chain, which is an improvement to the original model that only allows three trophic levels. Furthermore, the tool is flexible to modify food chain structure and the exposure scenarios for humans. Regarding parameters, the model requires *biomagnification factors* ($BMFs$) for each chemical, and the CSF and RfD to estimate potential health risks to humans. The Environmental Protection Agency has a database where these parameters can be found for a wide range of contaminants: the Integrated Risk Information System (IRIS) [30].

Thirdly, the code of the tool is open source. This has two straight-forward advantages with respect to the original model: 1) users can know how the model works, which equations are used, and even modify the code to incorporate additional capabilities to the tool, and 2) it can also be used as a stand-alone model called by other software.

However, the greatest contribution of Arc-BEST is that it enables the use of digital spatial datasets, allowing the user to perform spatial distributed risk analysis, which is a completely new capability of Arc-BEST. This also improves model creation speed compared to BEST when multiple sites are being analyzed. As the number of locations increases, the model creation speed decreases considerably. In addition, using a GIS software, significantly improves the comparison, analysis, and visualization of results with respect to the original tool. In the latter, the final risks are given in .pdf format, and hence, the users do not have the possibility to create their own graphs, map the spatial distribution of the risk, or incorporate other factors to the analysis, such as the population density used in this work.

The model also has some limitations. Firstly, it is an empirical model. This means that it uses statistical relationships. Although the definition of risk involves statistical concepts, the model has the disadvantage that it does not explain the mechanisms of the relationships, i.e., the cause-effect chain. The modeler has to account for the uncertainties in the statistical parameters that it uses, as detailed in Section 5.1.2.

Furthermore, the concentration of contaminants in species at the bottom of the food chain must be provided. The model cannot estimate this concentration based on environmental concentrations (i.e., in water or sediments) and conditions. However, since the code is open source, another model could be coupled to Arc-BEST to perform these calculations.

In addition, Arc-BEST is not time-varying. This means that it gives a “picture” of the risk based on the given concentration of contaminants in species at the bottom of the food chain. It does not consider potential decay or increase of concentrations. For instance, fate of contaminants can occur in the water column, their bioavailability can decrease if they settle to the bottom of the water body and get covered by new layers of sediments, or inversely it could increase if sediments are resuspended during an extreme event or during dredging activities.

Population dynamics is also not considered. The trophic chain defined by the modeler is considered to remain the same during the modeled period. In highly contaminated places this could not be a reasonable assumption, since populations of aquatic organisms could be affected by the levels of contaminants and get extincted from that location, or reduced to a few individuals. According to the case study, the modeler must consider if these assumptions are reasonable. Another way to address this limitation is to interpret the results as the potential levels of risk that humans would be exposed in the future given the current conditions in order to determine if restorative measures or more studies are needed.

Regarding ecological health, Arc-BEST's capability to analyze it is limited to the comparison of contaminant concentration in predator species to an ecological threshold. Although this threshold is contaminant-specific, it is not species-specific and it is not related to any specific risk or effect. This is an extremely simplified analysis. Therefore, when the threshold is exceeded we can conclude that the local ecosystem is potentially threaten by the presence of the contaminant under study, but further analyses and/or field data are needed to draw more specific conclusions and to help decision-making.

Finally, from the previous paragraph it can be inferred that the model cannot capture any specific effect of contaminants in organisms, such as the impact of a spike in contaminants concentrations in species populations and local ecosystems. With respect to human health it can only estimate risks due to long-term effects of contaminants, which are called chronic effects.

CHAPTER 6

CONCLUSIONS

6.1 Summary

In this work, a Python code with an ArcMap® interface is developed to perform bioaccumulation risk analysis. The tool is named Arc-BEST. It is based on the equations of BEST model, released by the USEPA and USACE in 2012 as part of the BRAMS software. The main contribution of the tool is that it enables the use of digital spatial datasets in order to perform spatially distributed risk analysis. Arc-BEST is easy to use and it increases model creation speed with respect to the original tool when several sites are being analyzed. Furthermore, it significantly improves the analysis, comparison and visualization of results. To put it in other words, the analysis of results becomes considerably more flexible, since in the original BEST model they are given in .pdf format, and therefore, the modeler does not have the possibility to create his/her own graphs, map the spatial distribution of the risk, or incorporate other factors to the analysis, such as population density, distance to contaminant sources, distance to urban centers, etc. Moreover, the code is open source. This way, users can know how the model works and are able to modify the code to incorporate additional capabilities to the tool. In addition, it can also be used as a stand-alone model called by other software.

Using Arc-BEST, the ecological and human health risks due to PCBs are studied in the Great Lakes region of the Midwest. PCBs are man-made organic chemicals, and are among critical contaminants in the Great Lakes. Following a screening-level risk assessment approach, the study is meant to be conservative and use minimal data. The latter justifies the use of total PCBs to characterize the risks, instead of specific congeners that could have different toxicity. Protective assumptions are made in the selection of the food chain, and in the definition of the consumption scenarios for humans, where an upper limit for body weight and exposure duration are considered to account for the uncertainties. The parameters that are used to estimate cancer risk and hazard index for humans (the CSF and RfD, respectively) also account for uncertainties in their definition. Based on historical data, it is concluded that assuming constant concentrations of PCBs in future years is a realistic assumption.

The ecological hazards are addressed comparing total PCBs levels in predator species with the ecological threshold of 4 ppm. For the round goby the threshold is not exceeded in any site, while for smallmouth bass it is exceeded in four sites: three in the west coast of Lake Michigan and one in Lake Ontario. Particularly, the estimated PCBs concentration in smallmouth bass in "Sheboygan River" site (Lake Michigan) is considerably high compared to the the rest of the locations, reaching 17 ppm, which indicates that the potential hazards are also great in this location. This result is consistent with the fact that this is a well known area of concern defined by the USEPA, and restoration measures have been recently applied in this area.

Regarding human health, cancer risk and hazard index (associated with non-cancer effects) are estimated based on long-term exposure to PCBs in the diet (from consuming contaminated fish from the lakes). Non-cancer effects seem to represent a greater hazard in the region than cancer risks. Considering that the average consumption of freshwater fish in the U.S. is approximately two meals per month, the analysis of the results is focused on a weekly consumer, in order to be conservative with the conclusions.

Overall, Lake Huron and Lake Ontario present the lower risks -due to PCBs- among all lakes. The upper bound of the hazard index does not exceed the recommended threshold for a weekly consumer, except in two locations: "Saginaw River" in Lake Huron and "Eighteenmile Creek" in Lake Ontario. More field data and analyses are needed in these two sites and in their surrounding area in order to identify which species are -or are not- safe to consume.

In Lake Michigan and Lake Erie the hazard index exceeds the threshold for all locations for a weekly consumer. However, in the former lake it is clear that the risk is greater in the west coast than in the east coast, where the upper part of the confidence bars exceed the threshold, but the mean values remain below it. In the east coast of Lake Michigan the risks due to PCBs do not seem to represent a great hazard for a monthly -or less frequent-consumer. On the other hand, for Lake Erie the risk seems to oscillate along the coast, and safer areas cannot be easily defined based on the risk distribution. In both lakes the potential risks due to the presence of PCBs cannot be rebutted, and high risks are not found to be isolated -on the contrary, vast areas of high risks are identified-. A more thorough analysis and more data are needed to further characterize the risk and potential effects on local ecosystems and human health, especially for vulnerable populations that are not addressed in this work, such as children and pregnant women.

6.2 Limitations

The greatest limitation of the case study is that other critical contaminants are not analyzed. Consequently, safe fishing areas cannot be identified from this study, even if the risk due to PCBs is low. Another limitation is that data is available only in the U.S. coast of the lakes. Given that atmospheric transportation could be an important source of PCBs in the Great Lakes, we cannot draw any conclusions regarding health risks in offshore locations.

Arc-BEST capability to analyze ecological health is extremely simplified, limited to the comparison of contaminant concentration in predator species to an ecological threshold, which is not species-specific and it is not related to any specific risk or effect. Therefore, when the threshold is exceeded we can conclude that the local ecosystem is potentially threaten by the presence of the contaminant under study, but further analyses and/or data are needed to draw more specific conclusions and to plan any restoration measure.

Another limitation is that it is an empirical model, and hence, it does not explain the mechanisms of the relationships. Moreover, Arc-BEST is not time-varying. This means that it gives a prospective "picture" of the risk considering the given concentration of contaminants in invertebrate species and the food chain defined by the user.

Finally, the tool is meant to estimate risks due to long-term effects of contaminants, so it cannot capture the impact of a spike in contaminants concentrations in local ecosystems or any acute effect on human health.

6.3 Recommendations

Arc-BEST can perform spatially distributed bioaccumulation risk analysis, helping decision and policy making. However, the modeler must understand its limitations and the simplifications in the underlying complex mechanisms that it tries to represent, which involves chemical, physical and biological processes. They are thoroughly described in Sections 5.2 and 6.2. The results should be analyzed based on the capabilities of the model and considering -and quantifying when possible- the uncertainties. In order to reduce uncertainty, the following points are suggested.

Firstly, it is crucial to collect enough -and good quality- samples of the study sites, which will depend on the characteristics of the environment, the organisms, and the contaminants under study. For zebra mussels in the Great Lakes, a few tens of individuals seem enough for each location [17]. Regarding free available data, the *Mussel Watch* program of the NOAA has very good quality. It uses up to 100 or more individuals for zebra mussels in the Great Lakes, 30 individuals for other mussels and 20 for oysters in other regions [55]. It also uses a performance based quality assurance process to ensure data quality [35].

Secondly, as important as the data collection is the definition of a proper food chain. It must represent a simplified but realistic trophic structure and pathway of contaminants to higher level predators in the local ecosystem. When available, it is preferable to use *biomagnification factors* ($BMFs$) from studies that are specific for the selected species and the location under analysis.

Thirdly, it is advisable that human exposure scenarios are defined using data from the region when available in order to realistically quantify the risks. Data of body weight, population mobility and fish consumption are generally available in a regional or national scale in the U.S. Some references used in this work that could be useful for other studies are the following: [46], [47], and [52]. Moreover, data of population mobility can be obtained from the U.S. Census Bureau (`https://www.census.gov/hhes/migration/data/cps.html`). Regarding the potential human health risks of contaminants, values for cancer slope factors and reference dose are available in the Integrated Risk Information System (IRIS) of the USEPA, and safety levels determined by the FDA can be found in [23].

In conclusion, Arc-BEST is a useful tool for screening-level risk assessment, as it was proved in this work. It enables to initially identify the hazards generated by contaminants and possibly rebut the presumption of risk. This way, it can contribute to make more informed decisions regarding restoration measures, monitoring of the sites under study, and collection of more specific data, ultimately enhancing humans' health and quality of life and protecting ecosystems. When the presumption of risk cannot be rebutted under conservative assumptions and considering the uncertainties of the study, it is advisable to use other bioaccumulation risk assessment models and perform field studies in order to improve robustness of the results and better characterize the risk.

6.4 Future Work

As stated before, the case study in this work is focused on the risks due to PCBs, which are among critical contaminants in the Great Lakes. Given free available data from the Mussel Watch Program of the NOAA, a screening-level risk assessment of all (or most) critical contaminants in the region could be performed. This study could potentially identify safe fishing zones and hot spot areas with high levels of risk. Another potential application of the tool that addresses a current threat to the Great Lakes region is described below.

Asian carps have infested much of the Mississippi River basin since escaping from southern fish farms some decades ago [56]. Currently, they are threatening to reach the Great Lakes [56–59]. They are invasive species without natural predators that compete with native species, which raises the concern of local authorities, the fishing industry, and researchers, among other social actors [57]. A consensus on the best solution to combat these species has not been reached [60, 61]. One proposed alternative is to foster fishing and human consumption of Asian carps as a management strategy to control their population [62, 63]. However, they could represent a potential hazard to human health due to bioaccumulation of contaminants. Some studies have detected accumulation of metals and other contaminants in samples of Asian carps collected from the Mississippi and Illinois rivers [64–66].

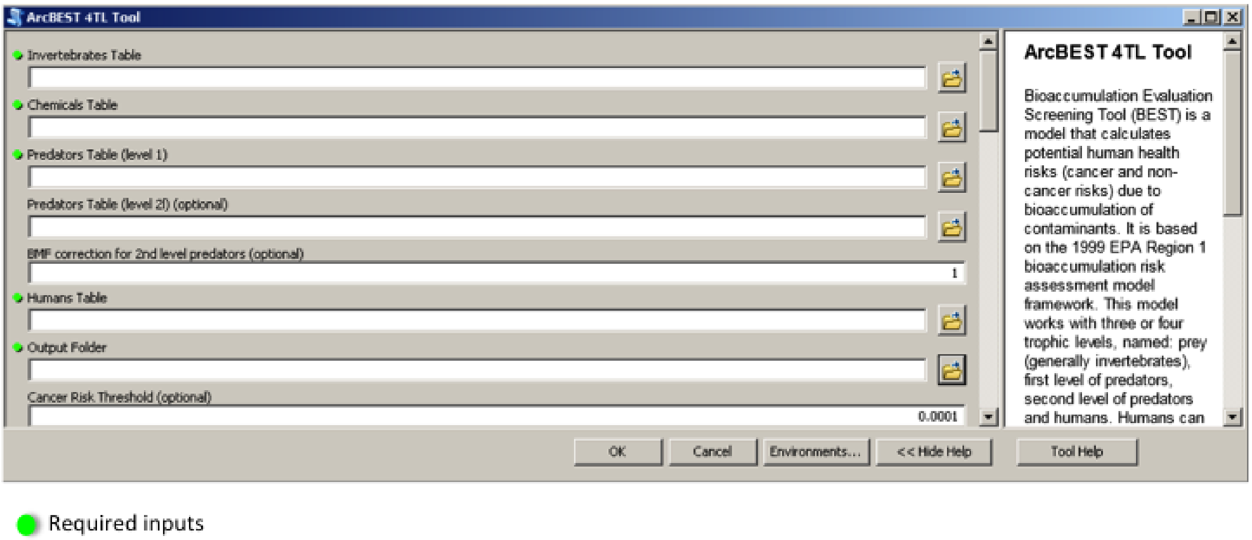
Arc-BEST tool would be useful to estimate human health risk due to consumption of these fish. The tool has the advantage that uses as input the concentration of contaminants in the diet species of the carps, which are mainly larger zooplankton, such as rotifers and crustacean zooplankton [67], avoiding the collection, handling and testing of fish. Particularly, it could be used to forecast the risk if the carps happen to invade the Great Lakes in a near future, allowing the local state governments to make a more informed decision on whether it is safe to foster the consumption of Asian carps to reduce their population.

APPENDIX A

ARC-BEST USAGE INSTRUCTIONS

A.1 Background

The purpose of this document is to provide usage instructions for Arc-BEST, which is a tool to perform spatially distributed bioaccmulation risk analysis. The source code of the tool is written in Python with an ArcMap® (by ESRI®) interface, shown in Figure A.1. Although the code can be used as a stand-alone model called by other software, the instructions below are for the ArcMap® application.


ArcBEST 4TL Tool

● Invertebrates Table

● Chemicals Table

● Predators Table (level 1)

Predators Table (level 2f) (optional)

BMF correction for 2nd level predators (optional): 1

● Humans Table

● Output Folder

Cancer Risk Threshold (optional): 0.0001

ArcBEST 4TL Tool

Bioaccumulation Evaluation Screening Tool (BEST) is a model that calculates potential human health risks (cancer and non-cancer risks) due to bioaccumulation of contaminants. It is based on the 1999 EPA Region 1 bioaccumulation risk assessment model framework. This model works with three or four trophic levels, named: prey (generally invertebrates), first level of predators, second level of predators and humans. Humans can

Figure A.1: Arc-BEST tool interface in ArcMap®, where required inputs are indicated.

A.2 System Requirements

Arc-BEST was created as a geoprocessing tool in ArcGIS® 10.1. It is proved to work with this and later versions of the software. The system requirements are then the same required for ArcGIS®, which can be found at `http://resources.arcgis.com/en/help/system-requirements/10.1/index.html#//015100000002000000`.

A.3 User Interface

As a geoprocessing tool, the user interface of Arc-BEST (see Figure A.1 follows the standard patter of ArcGIS® tools. The required inputs are the output folder where results are saved and tables with information of invertebrate species, chemical properties, predator species, and human exposure scenarios. They are indicated with green dots in Figure A.1. These are the minimum inputs that the user should specify. The tool also has several optional inputs, and a brief description of the model is available in the right panel of the interface. After uploading all the required information, Arc-BEST can be run by pressing the OK button located at the bottom of the interface.

A.4 Running Arc-BEST

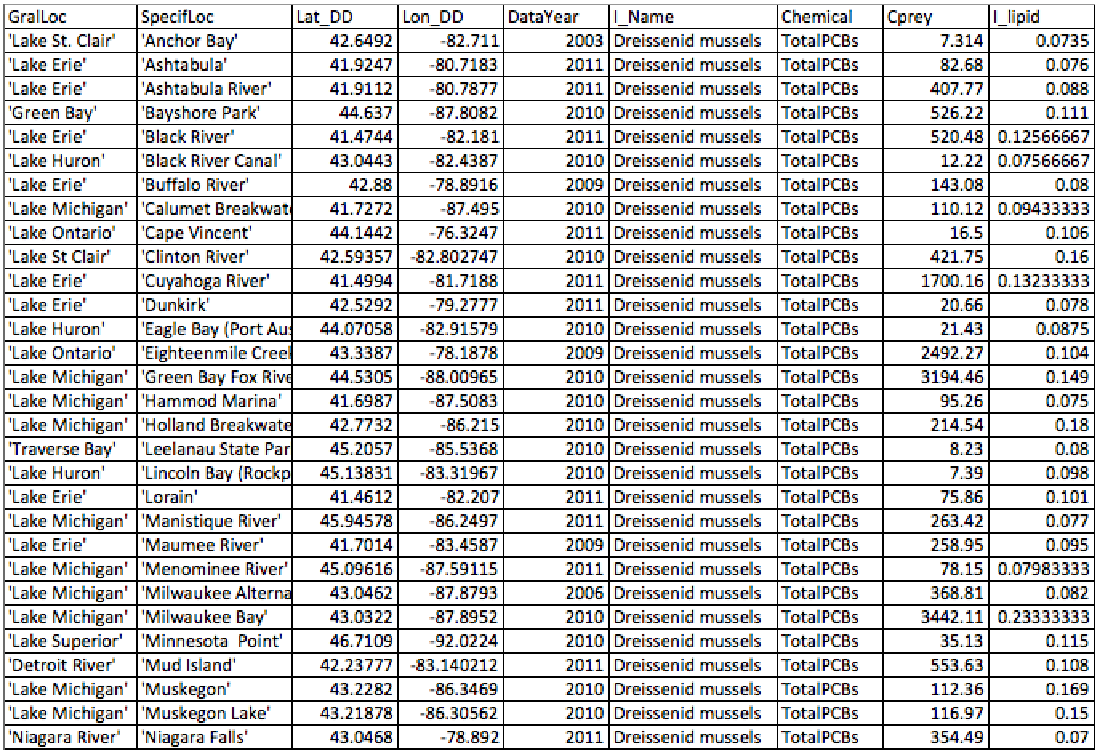
The basic usage of Arc-BEST includes specification of required inputs, specification of optional inputs (or leaving the default values), and running the model to get the results.

A.4.1 Required Inputs

Arc-BEST has five required inputs: four data tables with information related to invertebrates (preys), chemicals, first-level predators, and humans; and the output folder. The first four inputs are database tables and should have the extension .dbf, while the fifth input is the directory path and folder name where the results are going to be saved. The tables can be created in Excel and imported to ArcGIS® as a .dbf file using ArcCatalog®.

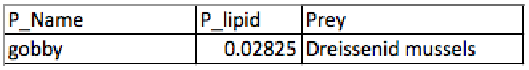
The minimum required fields in the input tables are described in Chapter 3 and presented in Tables 3.1 to 3.4 for invertebrates, chemicals, predators and humans, respectively. An example of each table can observed in Figures A.2 to A.4.

It is important to highlight that the input tables can contain multiple chemicals, multiple invertebrate and predator species, and multiple human exposure scenarios.



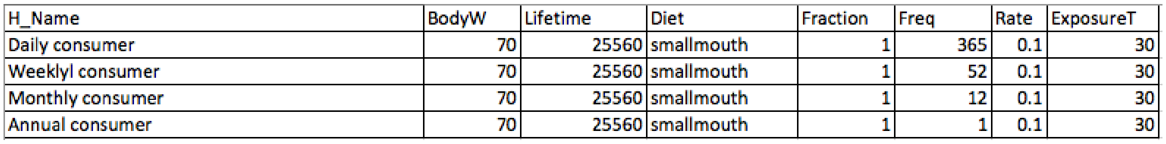
GralLoc	SpecifLoc	Lat_DD	Lon_DD	DataYear	I_Name	Chemical	Cprey	I_lipid
'Lake St. Clair'	'Anchor Bay'	42.6492	-82.711	2003	Dreissenid mussels	TotalPCBs	7.314	0.0735
'Lake Erie'	'Ashtabula'	41.9247	-80.7183	2011	Dreissenid mussels	TotalPCBs	82.68	0.076
'Lake Erie'	'Ashtabula River'	41.9112	-80.7877	2011	Dreissenid mussels	TotalPCBs	407.77	0.088
'Green Bay'	'Bayshore Park'	44.637	-87.8082	2010	Dreissenid mussels	TotalPCBs	526.22	0.111
'Lake Erie'	'Black River'	41.4744	-82.181	2011	Dreissenid mussels	TotalPCBs	520.48	0.12566667
'Lake Huron'	'Black River Canal'	43.0443	-82.4387	2010	Dreissenid mussels	TotalPCBs	12.22	0.07566667
'Lake Erie'	'Buffalo River'	42.88	-78.8916	2009	Dreissenid mussels	TotalPCBs	143.08	0.08
'Lake Michigan'	'Calumet Breakwat	41.7272	-87.495	2010	Dreissenid mussels	TotalPCBs	110.12	0.09433333
'Lake Ontario'	'Cape Vincent'	44.1442	-76.3247	2011	Dreissenid mussels	TotalPCBs	16.5	0.106
'Lake St Clair'	'Clinton River'	42.59357	-82.802747	2010	Dreissenid mussels	TotalPCBs	421.75	0.16
'Lake Erie'	'Cuyahoga River'	41.4994	-81.7188	2011	Dreissenid mussels	TotalPCBs	1700.16	0.13233333
'Lake Erie'	'Dunkirk'	42.5292	-79.2777	2011	Dreissenid mussels	TotalPCBs	20.66	0.078
'Lake Huron'	'Eagle Bay (Port Au	44.07058	-82.91579	2010	Dreissenid mussels	TotalPCBs	21.43	0.0875
'Lake Ontario'	'Eighteenmile Cree	43.3387	-78.1878	2009	Dreissenid mussels	TotalPCBs	2492.27	0.104
'Lake Michigan'	'Green Bay Fox Rive	44.5305	-88.00965	2010	Dreissenid mussels	TotalPCBs	3194.46	0.149
'Lake Michigan'	'Hammod Marina'	41.6987	-87.5083	2010	Dreissenid mussels	TotalPCBs	95.26	0.075
'Lake Michigan'	'Holland Breakwate	42.7732	-86.215	2010	Dreissenid mussels	TotalPCBs	214.54	0.18
'Traverse Bay'	'Leelanau State Par	45.2057	-85.5368	2010	Dreissenid mussels	TotalPCBs	8.23	0.08
'Lake Huron'	'Lincoln Bay (Rockp	45.13831	-83.31967	2010	Dreissenid mussels	TotalPCBs	7.39	0.098
'Lake Erie'	'Lorain'	41.4612	-82.207	2011	Dreissenid mussels	TotalPCBs	75.86	0.101
'Lake Michigan'	'Manistique River'	45.94578	-86.2497	2011	Dreissenid mussels	TotalPCBs	263.42	0.077
'Lake Erie'	'Maumee River'	41.7014	-83.4587	2009	Dreissenid mussels	TotalPCBs	258.95	0.095
'Lake Michigan'	'Menominee River'	45.09616	-87.59115	2011	Dreissenid mussels	TotalPCBs	78.15	0.07983333
'Lake Michigan'	'Milwaukee Alterna	43.0462	-87.8793	2006	Dreissenid mussels	TotalPCBs	368.81	0.082
'Lake Michigan'	'Milwaukee Bay'	43.0322	-87.8952	2010	Dreissenid mussels	TotalPCBs	3442.11	0.23333333
'Lake Superior'	'Minnesota Point'	46.7109	-92.0224	2010	Dreissenid mussels	TotalPCBs	35.13	0.115
'Detroit River'	'Mud Island'	42.23777	-83.140212	2011	Dreissenid mussels	TotalPCBs	553.63	0.108
'Lake Michigan'	'Muskegon'	43.2282	-86.3469	2010	Dreissenid mussels	TotalPCBs	112.36	0.169
'Lake Michigan'	'Muskegon Lake'	43.21878	-86.30562	2010	Dreissenid mussels	TotalPCBs	116.97	0.15
'Niagara River'	'Niagara Falls'	43.0468	-78.892	2011	Dreissenid mussels	TotalPCBs	354.49	0.07

Figure A.2: Example of an input table with invertebrate information.



P_Name	P_lipid	Prey
gobby	0.02825	Dreissenid mussels

Figure A.3: Example of an input table with first-order predator information.

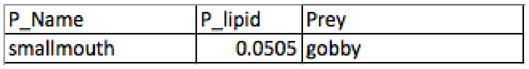


H_Name	BodyW	Lifetime	Diet	Fraction	Freq	Rate	ExposureT
Daily consumer	70	25560	smallmouth	1	365	0.1	30
Weeklyl consumer	70	25560	smallmouth	1	52	0.1	30
Monthly consumer	70	25560	smallmouth	1	12	0.1	30
Annual consumer	70	25560	smallmouth	1	1	0.1	30

Figure A.4: Example of an input table with human exposure scenarios information.

A.4.2 Optional Inputs

A data table with information regarding second-level predators is optional, giving the user the possibility to simulate three- and four-level trophic chains. The minimum information (fields) that this tabular dataset must contain is the same as the first-level predator table. An example is shown in Figure A.5.



P_Name	P_lipid	Prey
smallmouth	0.0505	gobby

Figure A.5: Example of an input table with second-order predator information.

The fields names in each tabular dataset are also optional inputs (format: text arrays). however, if the user does not specify them, they must match the default names or an error occurs when running the model.

Other optional inputs are the cancer and non-cancer risk thresholds (format: double), the default values are set equal to 1×10^{-4} for cancer risk and 1 for hazard index [11]. Finally, the correction for the BMF between the first- and second-level predators is also an optional input (format: double). See Chapter 3 for more information about this last parameter.

A.4.3 Outputs

After the required inputs are specified, the model can be run by pressing the OK button at the bottom of the tool's interface (Figure A.1).

The outputs are two (default) or three -when optional second-level predators are also specified- data tables (.dbf files), which are located in the output folder previously selected by the user.

One output table is called "inv_pred.dbf" and has, among other parameters, the concentration of contaminant in edible tissue of invertebrate species, the calculated concentration of contaminant in edible tissue of predator species, and the comparison between the latter with FDA action levels and with ecological effect levels through a Boolean expression: 0 if it does not exceed the levels and 1 if it does.

The second output table is named “inv_pred_hum.dbf”, and contains as a result the estimated $LADD$ (lifetime average daily dose, see Section 2.2) for humans based on the calculated chemical concentrations in their diet species, as well as the associated cancer risk and hazard index (non cancer risk), and the comparison between the risks and their respective thresholds through a Boolean expression.

If (optional) second-level predators are specified, a third output table is generated, named “inv_pred_pred2.dbf”. It contains the comparison between the concentration of contaminant in edible tissue of first- and second-level predator species with FDA action levels and with ecological effect levels. In this case, the first output table only contains the concentration of contaminant in edible tissue of invertebrate species and the calculated concentration of contaminant in edible tissue of first-order predator species.

Examples of these tables are shown in Figures 3.2 to 3.4. All the output tables contain other relevant information that was given as input by the user, such as the specific location identifier where invertebrate data samples where collected. Therefore, the tables can be easily converted to shapefiles or feature classes based on the latitude and longitude coordinates of the sites. Next, the user can map the results and apply any of the geoprocessing tools available in ArcMap® to analyze them.

A.5 Interpretation of Results

As mentioned before, multiple chemicals, invertebrate species, predator species, and human exposure scenarios can be included in the input tables of the tool. Figure A.6 shows the potential links between the different levels in the food chain. All the existent links should be specified by the user, i.e., the tool does not automatically assume them. Hence, first-level predators can feed on one or multiple invertebrates; second-level predators can feed on one or multiple first-level predators; and humans can consume one or multiple species form any -or both- of the predator levels.

The model does not add the concentrations or the risks at any moment during the calculation. So for a given number of chemicals c, invertebrates i, and first-level predators p, the **potential** number of results (rows) in "inv_pred.dbf" is $c \times i \times p$, which correspond to the calculated concentrations of each chemical in each predator tissue due to the consumption of each invertebrate species. Similarly, for a given number of second-level predators n, the **potential** number of results in "inv_pred_pred2.dbf" is $c \times i \times p \times n$; and for a given number of human exposure scenarios h, the **potential** number of results in "inv_pred_hum.dbf" is $c \times i \times p \times h + c \times i \times p \times n \times h$. These numbers are referred to one particular location, so the potential number of results could be incremented by the number of sites.

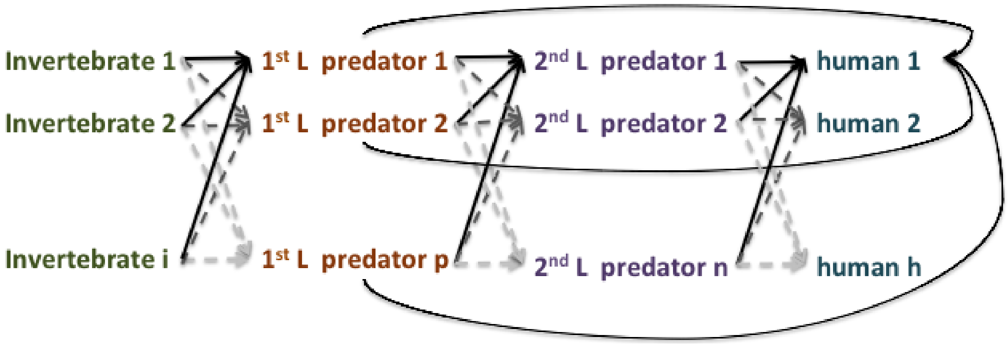


Figure A.6: Potential interactions between different levels of the food chain in Arc-BEST. Different arrow formats are just to improve visualization and do not have a special meaning. Similarly, the links between human 2 and human h categories with the 1^{st} L predator categories are not included to allow a clearer visualization of the other links.

The justification for not adding the risks is in first place -and most importantly-, not to loose information. As an example, the risks of a particular contaminant on human health due to consumption of different species could be added. But the information of which one represents a higher hazard, either due to higher biomagnification of the chemical or to consumption habits, would be lost. In addition, in some cases there is not enough information to know if adding is the proper procedure. For instance, interactions between different chemicals are not clear and the risk of consuming two different contaminants could be greater than just the sum of their individual risks. Another example is that the concentration of chemicals in predator species are calculated assuming that each prey species is their primarily diet species. Although adding the concentrations would be a protective assumption, the user might consider more appropriate to use an average or the maximum of them. As a summary, further summary of the results is left to the modeler criteria based on the case study and on the uncertainty of the input data.

APPENDIX B

EXPLORATORY ANALYSES OF POLYCHLORINATED BIPHENYLS CONCENTRATION IN ZEBRA MUSSELS

B.1 Temporal Evolution

The concentration of total PCBs in zebra mussels over time is presented in Figures B.1 to B.5 for Lakes Superior, Michigan, Huron, Erie, and Ontario, respectively. It can be observed from the left panels in these figures that in some locations the concentrations remain relatively constant over time, while in other they oscillate. However, a regular patter cannot be visually identified. By applying a Mann-Kendall test, the existence of monotonic trends are studied. With a 95% confidence level no trends are detected, and only two sites present trends with a 90% confidence level, which are decreasing. Both sites are located in the east coast of Lake Michigan. However, Mann-Kendall test better detects monotonic trends and the time series are short to get statistical significance.

The most updated (or recent) concentration is also compared with the mean concentration over the entire time period for each location, which are presented in the right panels of the figures. It can be observed that the most recent concentration is very similar to the mean concentration in a number of cases. For the remaining cases it is generally lower, except in Lake Michigan, where it is greater in various sites. The fact that the most updated value is lower than the mean for the entire period could indicate that, although the concentrations oscillate with time, they tend to decline, as it seems for “Leelanau State Park” (Figure B.1) or “Cape Vincent” (Figure B.5b). For other sites, such as “Olcott” (Figure B.5b) and “Niagara Falls” (Figure B.4) this does not seem to be valid. However, any decreasing or decreasing trend could be statistically proved in this study.

The most alarming (highest) concentrations in the last years occurred in Lakes Michigan and Erie, which are proved in this work to be the two lakes with greater risks, and in one site in Lake Ontario, also detected as a critical location in terms of risk.

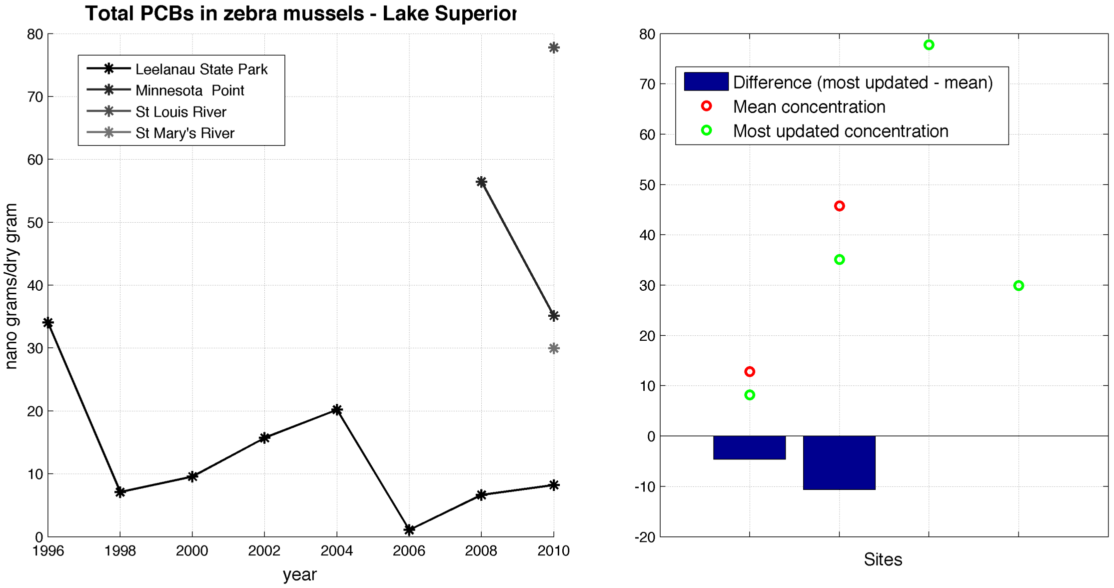


Figure B.1: Temporal evolution of PCBs concentration in zebra mussels in sites located in Lake Superior (left panel), and difference between mean and most updated (or recent) concentrations for each location (right panel).

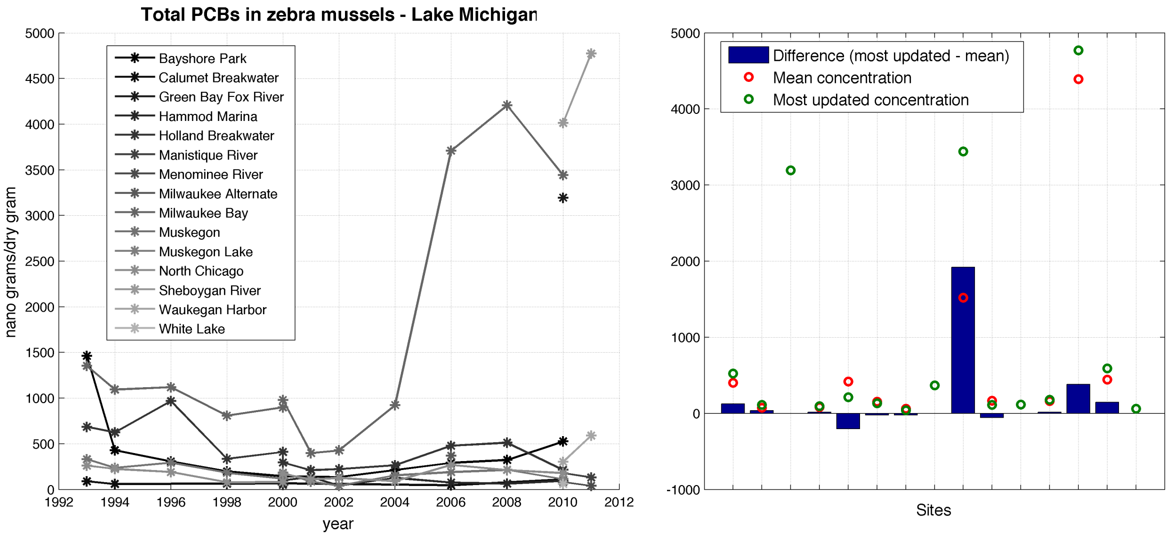


Figure B.2: Temporal evolution of PCBs concentration in zebra mussels in sites located in Lake Michigan (left panel), and difference between mean and most updated (or recent) concentrations for each location (right panel).

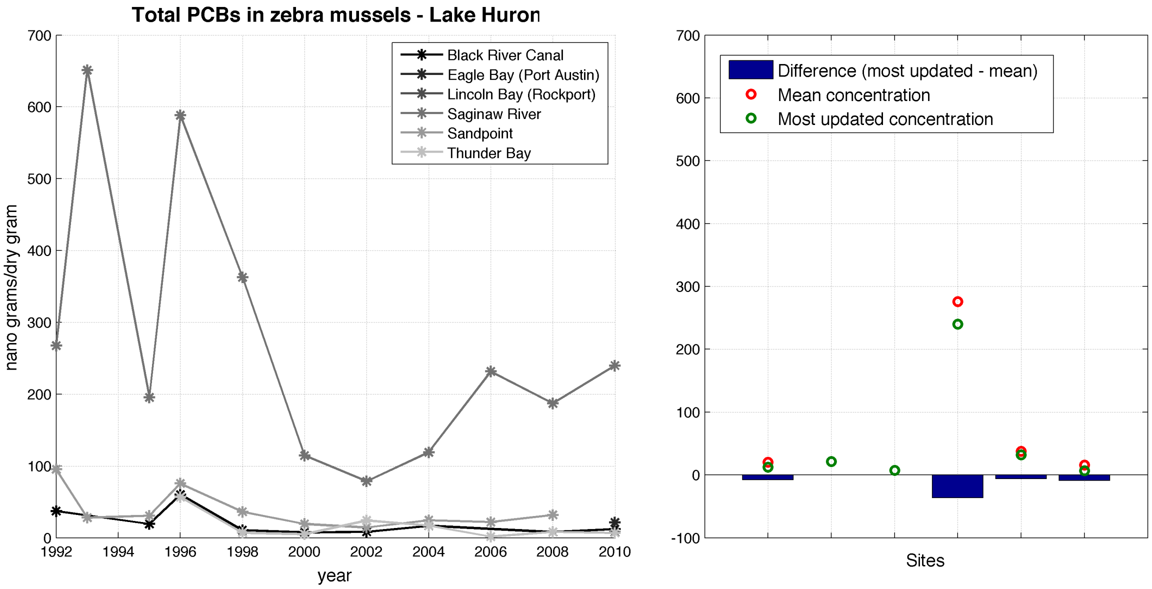


Figure B.3: Temporal evolution of PCBs concentration in zebra mussels in sites located in Lake Huron (left panel), and difference between mean and most updated (or recent) concentrations for each location (right panel).

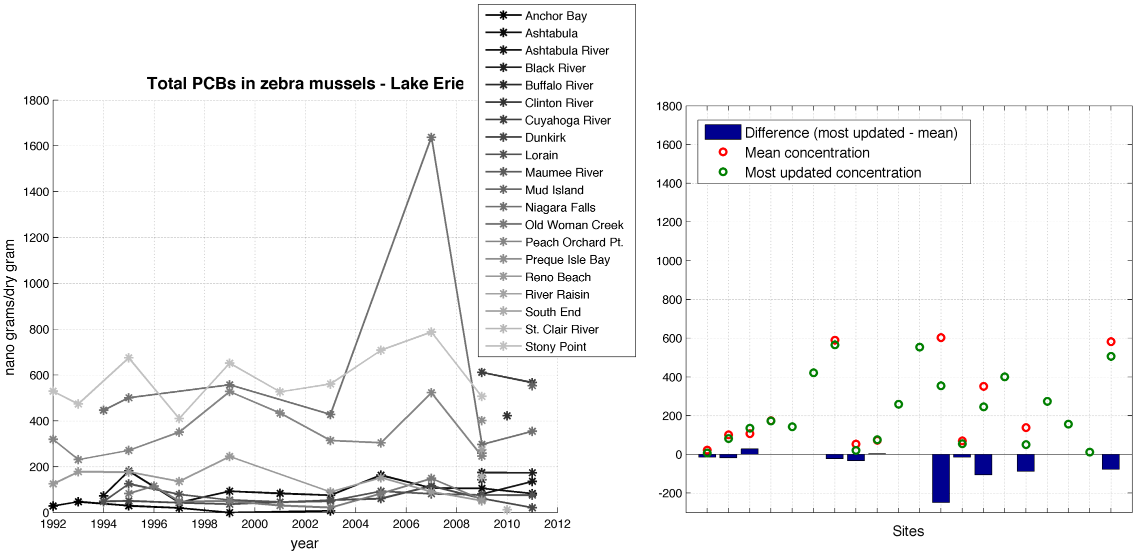
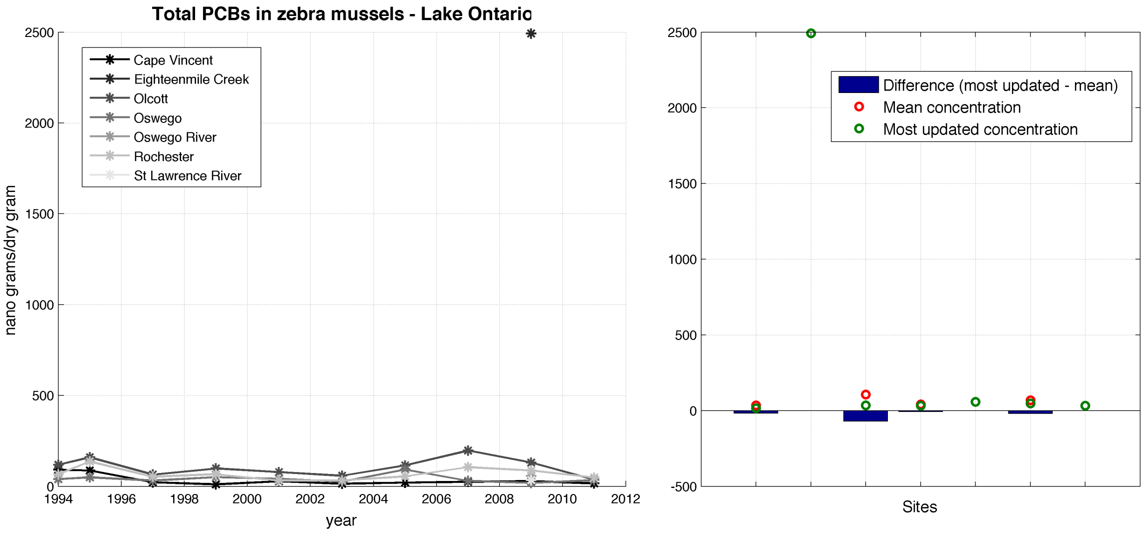
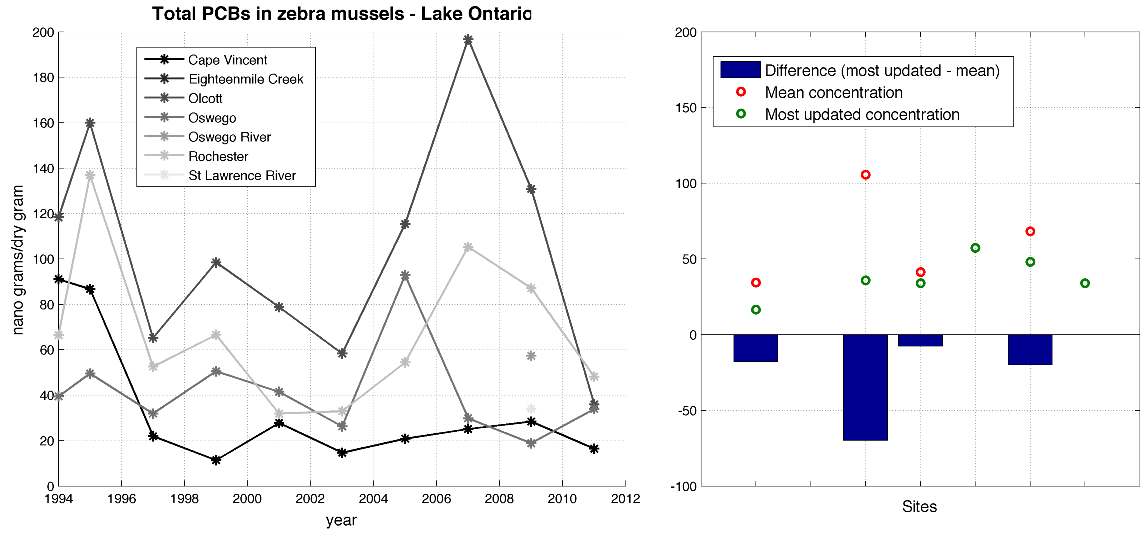


Figure B.4: Temporal evolution of PCBs concentration in zebra mussels in sites located in Lake Erie (left panel), and difference between mean and most updated (or recent) concentrations for each location (right panel).



(a) Including all sites in Lake Ontario.



(b) Zoom of Figure B.5a

Figure B.5: Temporal evolution of PCBs concentration in zebra mussels in sites located in Lake Ontario (left panels), and difference between mean and most updated (or recent) concentrations for each location (right panels).

B.2 Correlations with Lipid Content and with PCBs Concentrations in Sediments

Figure B.6 shows the concentration of PCBs in zebra mussels tissue versus their lipid content. PCBs are hydrophobic contaminants that tend to accumulate in lipids, so a high correlation was expected. Although the correlation of 0.32 is statistically significant, it is not very high, and a considerable amount of scatter can be observed in Figure B.6.

In addition, the concentration of PCBs in zebra mussels versus the concentration of PCBs in sediments is presented in Figure B.7. The correlation is not statistically significant and extremely low. This suggests that the mussels accumulate PCBs from water rather from sediments. Unfortunately, water concentrations of PCBs are not available in the locations under study.

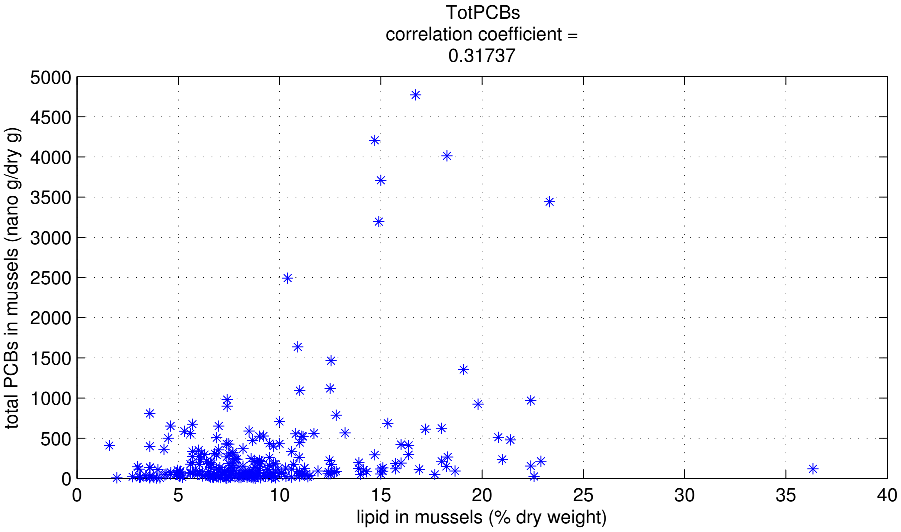


Figure B.6: Concentration of PCBs in zebra mussels tissue versus their lipid content.

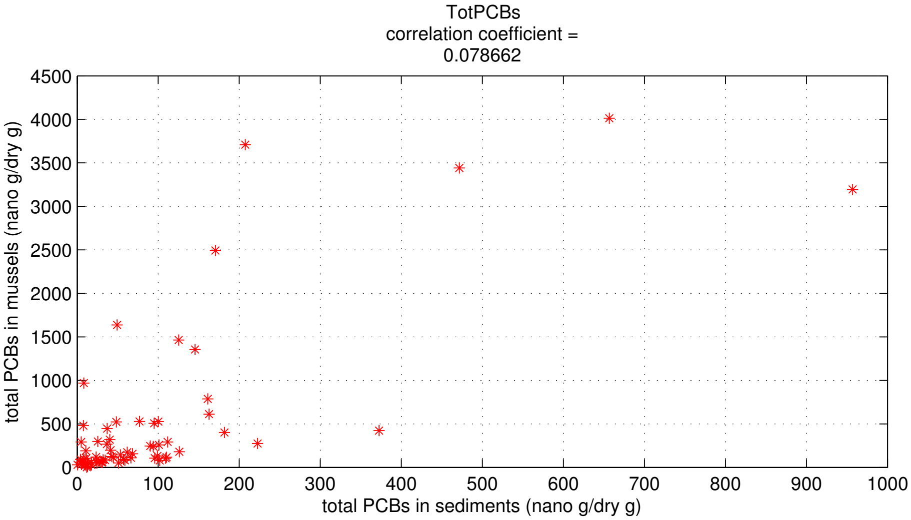


Figure B.7: Concentration of PCBs in zebra mussels tissue versus concentration of PCBs in sediments.

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