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Research article

A GIS-based tool for bioaccumulation risk analysis and its application to study polychlorinated biphenyls in the Great Lakes

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Abstract: This paper presents a GIS-based tool named 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, and corresponding bioaccumulation factors. Additionally, it estimates carcinogenic and non-carcinogenic risks for humans that consume those species. The greatest contribution of Arc-BEST is that it enables the automated use of digital spatial data sets, which improves model creation speed, analysis and visualization of results, and comparison and cross-referencing with other geographic datasets. Furthermore, the model was improved to consider up to four trophic levels. The code is written in Python and is open-source. In this work Arc-BEST is 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 in the Laurentian Great Lakes, where long-term effects of polychlorinated biphenyls (PCBs) is performed, based on measured concentrations in zebra mussels (*Dreissena polymorpha*), and local bioaccumulation factors from previous studies. 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 various exposure scenarios. The distribution of the risks in the lakes is analyzed, and critical areas are identified.

Keywords: bioaccumulation; risk analysis; GIS; PCBs; Great Lakes; zebra mussels

1. Introduction

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 [1]. They can represent potential risks for human health and for both aquatic and terrestrial ecosystems due to the mechanism of bioaccumulation. Bioaccumulation happens when the rate of intake of a certain compound by an organism from water or food exceeds the removal rate, and can attain concentrations several orders of magnitude greater than their aqueous concentrations [2–4]. Furthermore, sediments can serve both as a sink and reservoir of contaminants, entering the aquatic food web through benthic organisms [5–8]. 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 [7,9]. Because humans are at the top of the food chain, the health risks for consuming contaminated species can be magnified.

The objective of this work is to develop a Geographic Information System (GIS)-based tool to estimate bioaccumulation of contaminants in aquatic ecosystems, and the health risks for humans that feed on these species. The tool, named Arc-BEST, is used in the study of risks to local aquatic ecosystem and population posed by PCBs in the Great Lakes region of the Midwest. Knowing the magnitude of the risk 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. A clear example is the elaboration of safe fishing guides and update of fish consumption advisories, which currently exist for some fish in the Great Lakes [10].

1.1. The tool

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]. BRAMS is a stand-alone tool for calculating the potential human health and ecological risks associated with bioaccumulation of contaminants. It includes two 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 [12]. Arc-BEST 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. It has several strengths: it is easy to use, requires few parameters, and it has flexibility to modify the food chain structure and exposure scenarios. However, it 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.

GIS can add extremely valuable resources to a risk analysis assessment, facilitating the incorporation of social-cultural, economic, 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 found in [13–17]. In these studies GIS has proved to be a very effective tool to handle spatially arrayed data, to better analyze the spatial distribution of hazards, and generate risk maps, which are useful in decision-making processes concerning environmental pollutants. Combining the strengths of the original BEST tool with the numerous capabilities of GIS, an open source 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. 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. Arc-BEST enables the automated use of digital spatial data sets, which 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 model. We propose to use it as part of screening-level risk assessment process, in order to identify hot spots where further studies and monitoring should be performed to ensure human and ecosystem health. The tool is successfully applied to a case study of PCBs in the Great Lakes.

1.2. The case study

The Laurentian Great Lakes are one of the largest fresh surface water systems in the planet, covering more than 94,000 square miles and draining more than twice as much land [18]. 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 [10]. However, persistent bioaccumulative toxic chemicals have affected water quality, and contaminated fish, impacting the entire ecosystem. PCBs are among these critical contaminants in the Great Lakes [19,20]. 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.

1.2.1. Properties, sources, and effects of PCBs

PCBs are aromatic compounds that can have between 1 and 10 chlorine atoms substituting for hydrogen atoms in the biphenyl rings, forming up to 209 different congeners [21]. Their 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. Their commercialization was banned in the United States in 1979. Between those years, around 700,000 tons of PCBs were produced in the U.S., and almost 90% were used domestically [21]. The recycling of PCB-contaminated products can keep PCBs in circulation for many years. According to the USEPA, between 1998 and 2011, 45,800 tons of PCBs were registered to remain in service in electrical equipment [22].

Once in the environment, PCBs are slow to biodegrade and are generally persistent in all media because of biogeochemical cycling in the aquatic environment [21]. Particularly, they are relatively stable in the atmosphere and therefore, they are subject to atmospheric transportation [23]. Atmospheric deposition was attributed as the primarily source of these toxics in the Great Lakes [24]. 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 [24]. Chicago seems to be a source of atmospheric concentrations of PCBs to Lake Superior, and a possible source to the east coast of Lake Michigan [23,24]. More recently, Melymuk et al. [25] studied loadings from different organic contaminants from Toronto to Lake Ontario. They found that atmospheric deposition 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 [21]. 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 [21].

The primarily means of exposure to both wildlife and humans is through the food chain due to the bioaccumulation an biomagnification capacity of these chemicals, and this is particularly true in the Great Lakes region [26,27]. 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 [21,28]. A thorough review of effects of PCBs on development and reproduction of humans and animals can be found in [29]. 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, because of data availability only total PCBs concentrations were used, which is believed to be a reasonable approach for a screening-level risk assessment [21].

1.2.2. Exposure pathway

Zebra mussel (*Dreissena polymorpha*) is an invasive species that by 1990 had infested all the Great Lakes [30]. The mussels have a high filtering capacity, the tendency to feed on sediments and algae [31], and high bioconcentration rates [32]. Consequently, contaminants previously destined for sediments can be redistributed, increasing contaminant bioavailability and the potential transfer of these contaminants to higher levels in the trophic chain [33–35]. For this reason, and the availability of data, zebra mussels are selected as the prey species in this study.

Several sport fish that are potential predators of zebra mussels are identified in the Great Lakes. They are: yellow perch and freshwater drum [33], lake whitefish [36], lake sturgeon and catfish [37]. However, the risk could be underestimated when the trophic chain involves other predator levels, as the case of the round goby (*Neogobius melanostomus*) that consumes zebra mussels, and it is a prey of the smallmouth bass (*Micropterus dolomieu*) [31]. In order to take a more realistic—and also protective—assumption, 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 [35]. 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 predator, since field and experimental data suggest that round goby is their preferred prey [35]. The zebra mussel-round goby-smallmouth bass is a typical aquatic food chain in the Great Lakes. Shore birds and terrestrial mammals, as well as humans, could be exposed to PCBs through the consumption of these species.

2. Data and methods

2.1. Model equations

The original BEST model considers a three-level food chain: invertebrates, predators, and humans. In Arc-BEST, an additional trophic level is incorporated, which allows the user to create a more realistic 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,

$$C_{pred} = \frac{C_{prey}}{NF} \times BMF \times \frac{Lipid_{pred}}{Lipid_{prey}} \tag{1}$$

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} is typically in µg/g for metals and in ng/g for organic contaminants, thus *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, where standard testing duration is shorter than natural exposure periods. The biomagnification factor *BMF* accounts for accumulation of chemicals in predator's tissue from consumption of the prey species. Chemicals that biomagnify, or increase their concentration up the food chain, will have *BMFs* > 1.

The result from Eq (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:

$$LADD = \frac{C_{pred} \times FI \times F \times IR \times ED}{BW \times LT} \tag{2}$$

where *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*) as follows,

$$Cancer\ Risk = LADD \times CSF \tag{3}$$

According to USEPA [38], this approach is based on the thinking that cancer effects lack a threshold, and that the risk increases linearly with a slope given by the *CSF*. This linear approach is used for direct-acting carcinogenic agents, or when there are insufficient data to demonstrate that the mode of action of the chemical is nonlinear.

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:

$$Hazard\ Index = \frac{LADD}{RfD} \quad (4)$$

where the *RfD* corresponds to the daily exposure that will likely not generate harmful effects during a lifetime [39]. Doses less than the *RfD* are probably not associated with adverse health risks. The uncertainty of the *RfD* spans about one order of magnitude [39]. A hazard index greater than 1 is considered indicative of potential health effects, while for cancer risks, an acceptable risk upper bound between 1×10^{-4} and 1×10^{-6} is typically applied [12]. 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 [40] and with ecological effect levels when available.

Arc-BEST is able to perform the equations presented above for several locations, which are usually associated with the places where invertebrate (prey) samples are collected. Further description of the tool can be found in the supplementary information and in [41].

2.2. Approach

In this work we perform a screening-level risk assessment to identify the degree of risk posed by PCBs in the Great Lakes region. A screening-level risk assessment 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 [21]: (i) the degree of contamination is small and poses no significant risk; (ii) the risk is estimated to be relatively great but the extent of contamination is relatively small; and (iii) potential risks cannot be rebutted and the extent of contamination is relatively great. In the second case, a particular risk-management strategy could be identified as feasible and cost effective without further refinement of the risk assessment, while in the latter more thorough studies should be conducted.

The assessment process has the following steps: (1) hazard identification, (2) exposure assessment, (3) effects assessment, and (4) risk characterization [42]. The first step, hazard identification, involves the general site and contaminant characterization. Moreover, the links between contaminant sources and receptors should be defined. The second step, exposure assessment, requires quantifying exposure characteristics of human and ecological receptors identified in the previous step. Effects assessment is the third step, where the potential toxicity of contaminants should be addressed. 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.

The first step of the process, i.e., hazard identification was already addressed in the Introduction (Section 1.2), while the second and third steps are addressed below. The last step corresponds to the results obtained using Arc-BEST, which are presented in Results and discussion (Section 3.1).

2.2.1. Data

Concentration of total PCBs in zebra mussels (*Dreissena polymorpha*) were obtained for 52 locations in the Great Lakes, indicated in Figure 1, from the National Status and Trends Mussel Watch Program of the NCCOS, NOAA (National Center for Coastal Ocean Science, National Oceanic and Atmospheric Administration). Datasets from Mussel Watch Program can be downloaded at no cost from http://egisws02.nos.noaa.gov/nsandt/index.html#, where total PCBs concentrations in zebra mussels are available. The data selected was the most recent available at the time the study was performed, which was 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. Mussel Watch Program uses a performance based quality assurance process to ensure data quality [43]. Therefore, good quality of the data is assumed. Nevertheless, some exploratory analyses were performed. The sampling protocol and methods are described in [44,45].

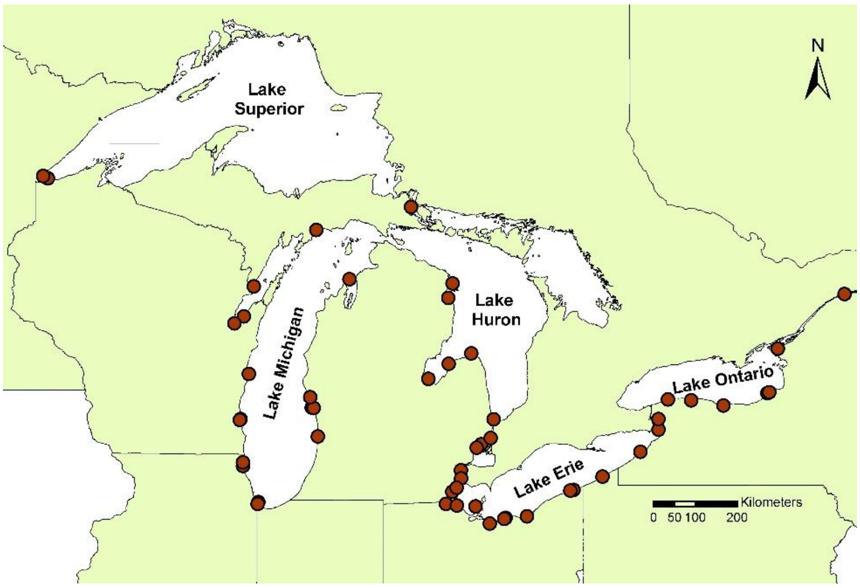


Figure 1. Locations in the Great Lakes where concentration of PCBs in zebra mussels were obtained.

The presence of trends was studied. For most locations, concentrations from 1992–1994 and up to 2009–2011 were available typically every other year. To determine the existence of trends, Mann-Kendall test [46] was applied to total PCBs concentrations in each of the 52 locations, with a confidence level of 95%. None of the locations presented any increasing or decreasing trend. Moreover, with a confidence level of 90%, only two sites were detected to have a decreasing trend, both located in the east coast of Lake Michigan. However, Mann-Kendall test better detects monotonic trends [46], and the time series are short to get statistical significance (at most 11 years of data were available for a given site). There are some recent studies that have found decreasing trends of PCBs in Great Lakes' fish. The work of [47] shows significant declines in PCBs in fillet portions of lake trout and whitefish over the past 20 years, while [48] 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. The most recent concentration was compared with the mean concentration over the entire time period for each location (not shown). They were both very similar for many sites. For the remaining ones, the most recent concentration was generally lower than the mean concentration, except for a couple of exceptions. From this analysis, there was no evident justification for selecting any concentration over another. Therefore, the most recent value was assumed to be a reasonable selection.

2.2.2. Exposure assessment

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 these species. Arc-BEST can address ecological risks by comparing contaminants concentrations in predator species (round goby and smallmouth bass) with ecological thresholds. This is a simplified approach, since it is not possible to define specific exposure characteristics for other ecological receptors.

On the other hand, the tool allows to define detailed exposure scenarios for humans. The data required to characterize human exposure scenarios 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 0.1 kg/day. Rather than fixing the frequency, different scenarios are considered in order to evaluate the health risks based on the ingestion frequency. They are presented in Table 1.

Table 1. Fish consumption 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 was selected as 20 years in this study. Nevertheless, as this parameter is uncertain, lower and upper bounds of 1 and 60 years were considered to estimate error bars. The upper limit of 60 years is 75 % of the life expectancy in the U.S., which is equal to 80 years [49]. 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 error bars. The weight of female adults in the 5th percentile is selected as the lower limit, while the weight of male adults in the 95th percentile is considered as the upper bound. These values are equal to 50.5 kg and 122.6 kg, respectively [50]. Finally, lifetime is estimated based on life expectancy at birth in the U.S., which is equal to approximately 80 years (29,200 days) [49].

2.2.3. Effects assessment

The concentrations in predators' tissue are calculated based on biomagnification factors (*BMFs*). The *BMF* is defined as the ratio of the lipid-normalized concentration of the chemical in the predator to the lipid-normalized concentration in the prey. Kwon et al. [35] 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 region of the Great Lakes, the *BMFs* between these species are calculated using the average of the four sites. From mussel to round goby, the *BMF* is equal to 1.57, while from round goby to smallmouth bass, a *BMF* of 2.53 is obtained. The lipid content for both round goby and smallmouth bass are also obtained from [35], while for zebra mussels the lipid content is obtained from the Mussel Watch Program of the NOAA.

To evaluate potential ecological adverse effects, an upper threshold is used. The estimated PCBs concentration in predator tissues (round goby and smallmouth bass) are compared with an ecological effect threshold. This threshold is a contaminant-specific upper bound, but it is not species-specific. For total PCBs, a value of 4 mg/kg is considered according to [11].

To assess risks for humans, the simplest approach is to compare the concentration of PCBs in smallmouth bass with the FDA safety level of 2 mg/kg [40]. This gives an idea of risk hot spots before considering any exposure scenario. A somewhat 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 described in Section 2.1. The *CSF* and the *RfD* are obtained from the EPA Integrated Risk Information System (IRIS) [51]. The *RfD*, equal to 2×10^{-5}, is based on a commercial mixture of PCBs (Aroclor 1254), which has a medium confidence level and uncertainty factor (already applied) in the order of a few hundreds. For food chain exposure, which is considered as high risk and high persistence, a *CSF* of 2 is defined. Finally, human risks estimated based on *CSF* and *RfD* are compared to recommended thresholds. For cancer risks, a value of 1×10^{-4} is considered, while for hazard index a value of 1 is used, both based on [11]. 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 safe to consume fish at a given ingestion rate, regarding PCBs contamination. The cancer risk threshold can be further 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, and it is computed as 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 is not safe to consume fish at a given ingestion rate.

3. Results and discussion

3.1. Risk characterization

Using the information from 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. In addition to assumptions already stated, it is considered that all organisms feed and remain at each of the sites. This is true for sessile mussels, but it is an assumption for fish species. According to [35], round goby is a territorial species and mobility of smallmouth bass is limited, only 1 to 3 km during multiple-season field studies. All sites are more than 3 km apart.

The comparisons between concentration of total PCBs in predators' tissue with FDA safety level of 2 mg/kg and ecological effect level of 4 mg/kg are presented in Figure 2. Figure 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 another one in Lake Ontario. These sites are located near relatively high populated areas, usually between 100 and 1000 people per square mile. Furthermore, three of them are very close to important urban centers (with more than 1000 people per square mile), such as Chicago (south location at Lake Michigan), Cleveland (Lake Erie), and Rochester (Lake Ontario). The magnitude of PCBs concentration in predators' tissue is presented in Figure 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. The highest concentration occurs in "Sheboygan River", very close to the city of Sheboygan, where it reaches a value of 17 mg/kg. This concentration is about 4.25 times that of the Ecological effect level, and 8.5 times when compared to the FDA safety level. With the parameters described in Section 2.2.2 (considering average body weight and exposure time of 20 years), the safety level of 2 mg/kg corresponds to a cancer risk of 1.3×10^{-3}, 1.8×10^{-4}, 4.2×10^{-5}, and 3.5×10^{-6} for the different consumption scenarios (daily, weekly, monthly, and annual); while the hazard index is 31.9, 4.6, 1, and 0.1, respectively. Considering thresholds of 1×10^{-4} for cancer risk and 1 for the hazard index, it can be observed that the FDA safety level is safe in terms of health risks for the two least frequent consumption scenarios, i.e., monthly and annual consumers. The risk is proportional to fish concentration of PCBs, and therefore in Sheybogan River the risks are 8.5 larger than these ones.

The results of human health risks for all the sites are presented in Figures 3 to 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 relative risk level, 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.

Figure 3a shows that in Lake Michigan the highest health risks are estimated in the west coast of the lake. This can also be observed in Figure 3b, where the same sites are sorted from west to east and from north to south. Overall it is potentially safe to consume fish only once per year or less frequently. 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. Besides "Sheboygan River", which is near the city of Sheybogan, other sites with high risks that are located near important urban centers are "Waukegan Harbor", "Milwaukee Alternate", and "Milwaukee Bay". In these areas, the population density is more than 1000 people per square mile.

(a)

(b)

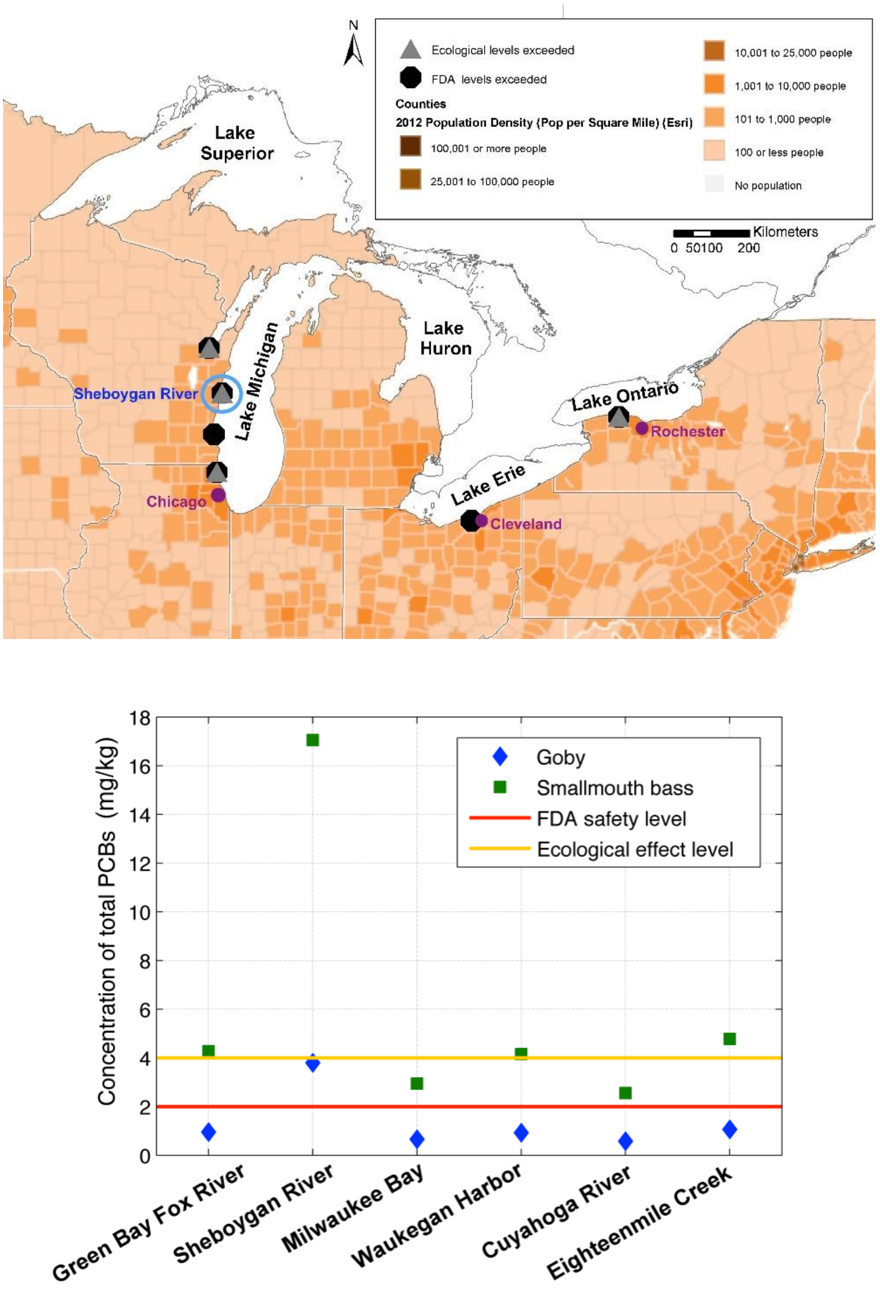


Figure 2. (a) Locations where FDA safety level (black dots) and ecological effect level (grey triangles) are exceeded in smallmouth bass tissue. U.S. population density in the is presented, as well as important urban centers close to the sites. The most contaminated site, Sheybogan River, is also indicated in the map. (b) Concentration level of total PCBs in round goby (diamonds) and in smallmouth bass (squares) for the map locations in a), sorted following the coastline from west to east and from north to south. The concentrations are expressed in mg/kg (wet weight basis). FDA safety level and ecological effect level are also shown (solid lines).

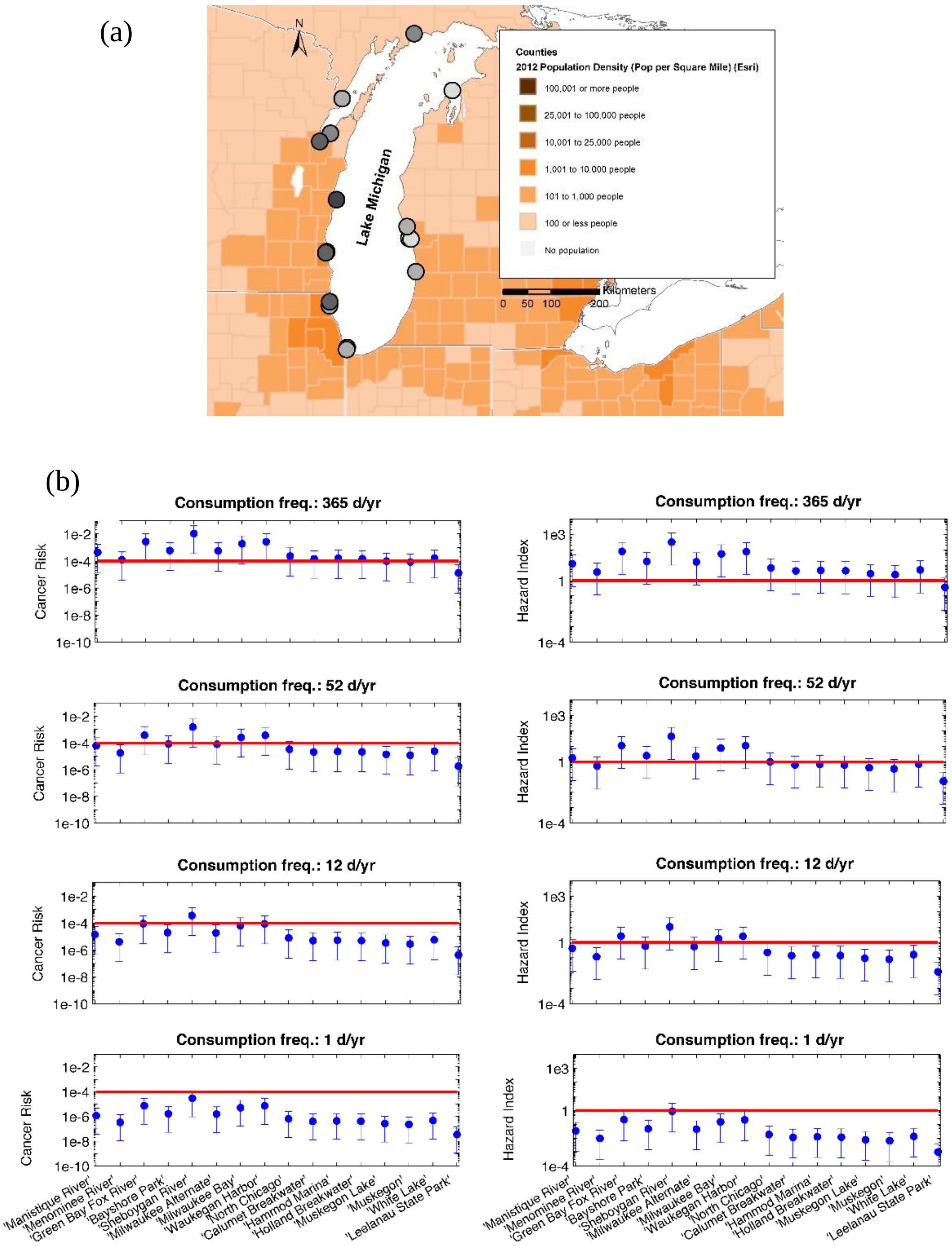
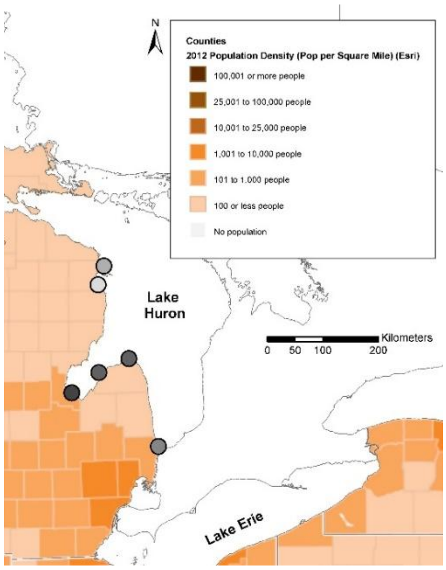


Figure 3. (a) Study sites in Lake Michigan, where darker colors indicate higher health risks. U.S. population density is also presented. (b) Cancer risk (left) and hazard index (right) levels based on consumption frequencies for the map locations in (a), sorted following the coastline from west to east and from north to south. Upper and lower bounds for the risks are presented. Risk thresholds are also indicated (solid lines).

According to Figure 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 4b). It is important to highlight that this site is located near a relatively high populated area, with 100 to 1000 people per square mile. Considering the average risk, an ingestion rate of 365 days/year is potentially safe in the sites of Lake Huron (except for "Saginaw River").

(a)



(b)

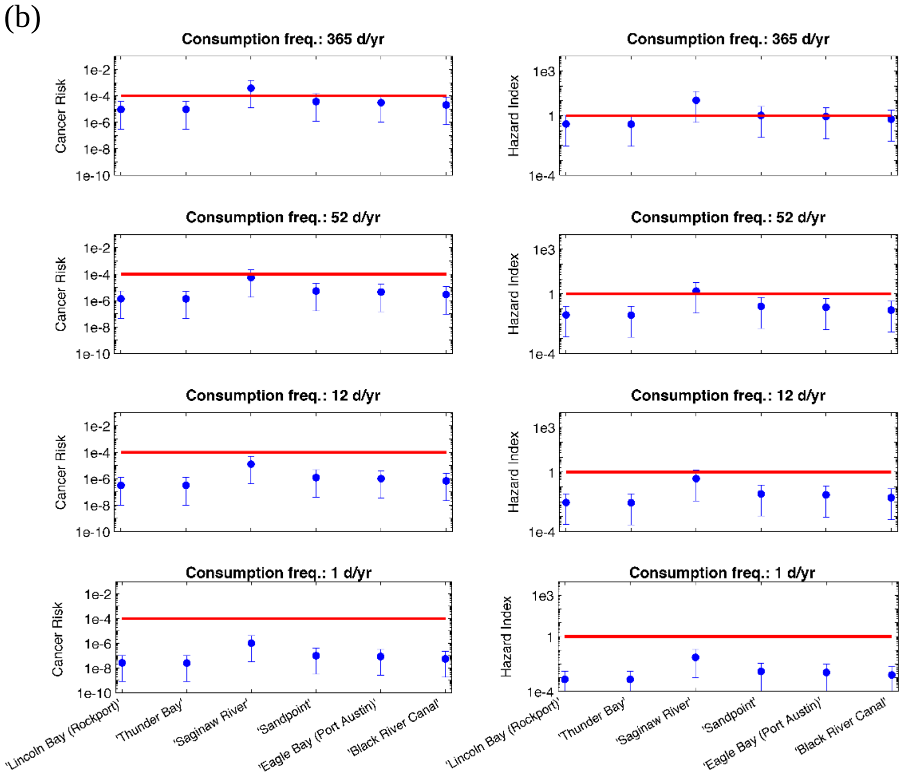


Figure 4. Same as Figure 3 but for Lake Huron.

In Lake Erie, it is difficult to identify safer fishing areas from Figure 5a due to the number of sites in this lake. However, from Figure 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. However, almost all the sites exceed the risk thresholds for an ingestion rate of 365 days/year. Regarding population density, the entire coast of this lake is relatively highly populated, with population rates between 100 and 1000 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 Detroit and Toledo (east coast of Lake Erie).

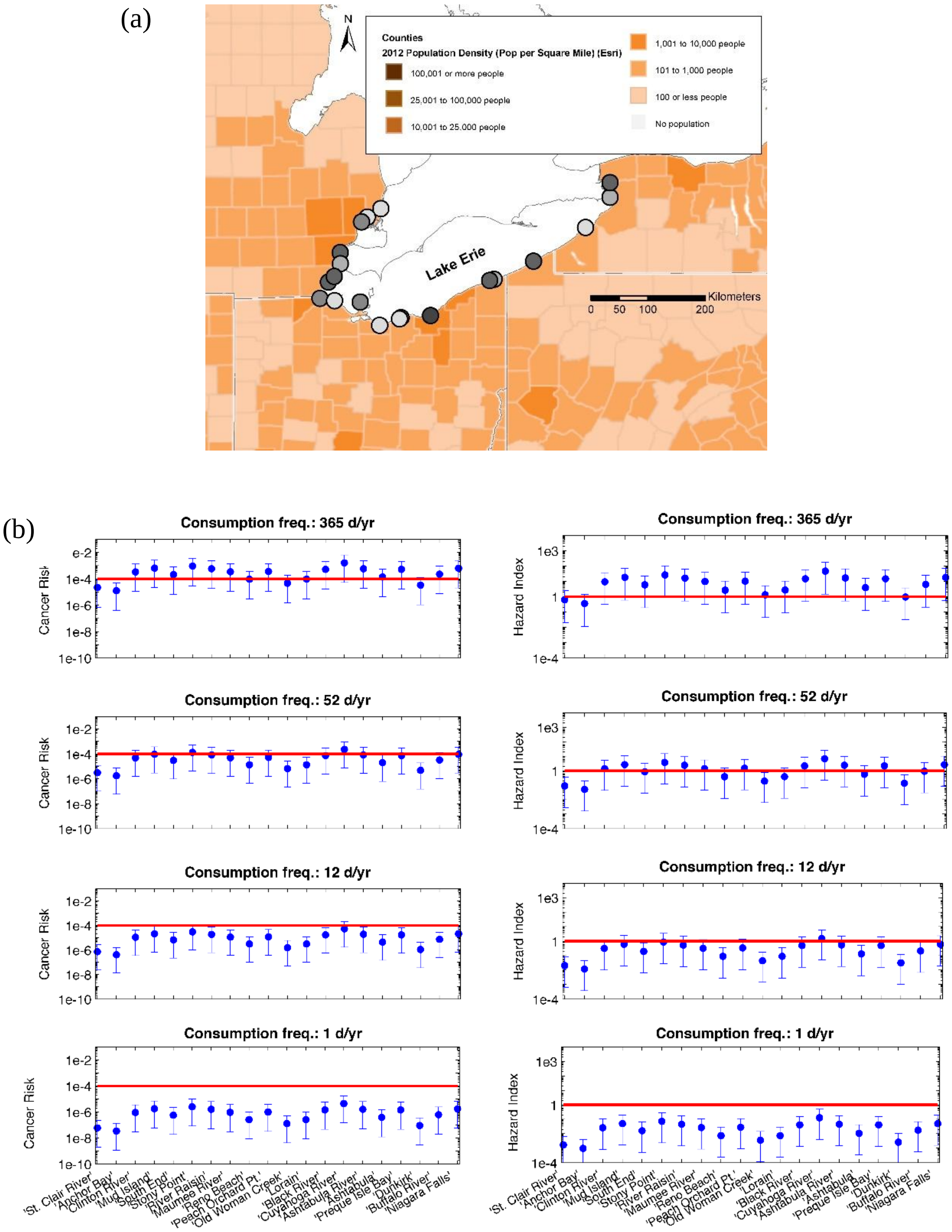


Figure 5. Same as Figure 3 but for Lake Erie.

For Lake Ontario, the risk levels do not seem to follow any clear pattern (Figure 6a). On the other hand, from Figure 6b it can be observed that there is one site with considerably higher risk values, which is “Eighteenmile Creek”. Here, the risk thresholds are exceeded for a consumption rate of once per month. In the remaining sites, a consumption rate of once per week seems to be safe regarding PCBs toxicity. The coast of Lake Ontario is also relatively densely populated, being Rochester the main urban center in the U.S. coast. “Eighteenmile Creek” is not very far from this area.

Overall, from Figures 3 to 6, it can be observed that 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.

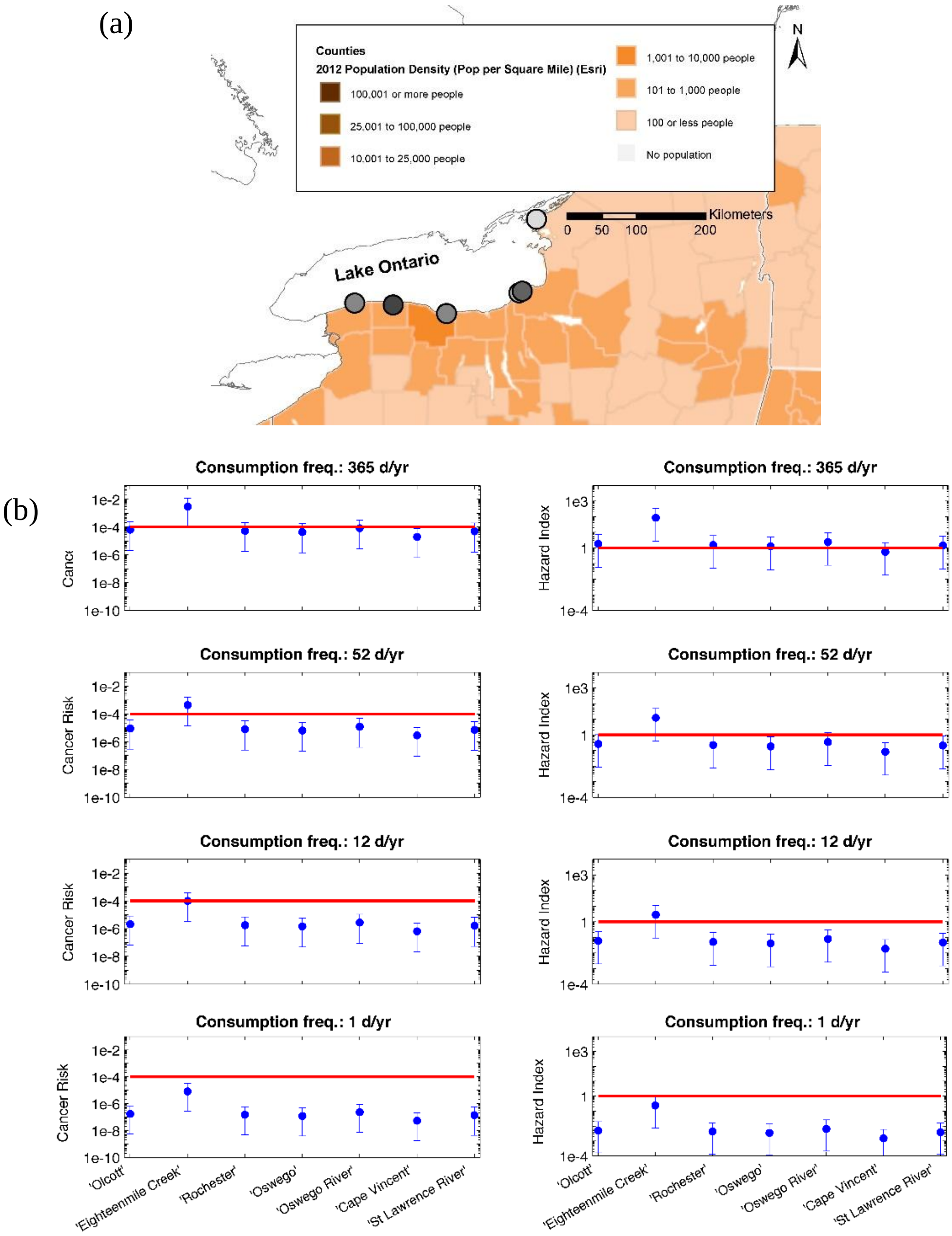


Figure 6. Same as Figure 3 but for Lake Ontario.

3.2. 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 mg/kg. 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 2a. There is one particular site where estimated PCBs concentration is considerably higher (4 to 8 times) than in the other five sites, which is "Sheboygan River". As indicated before, historical sources of PCBs to the Great Lakes were industrial plants, while current sources could be atmospheric deposition, illegal disposal of PCB-containing products and leaks from hazardous waste sites or old factories. In Sheboygan River, the main source of PCBs was a former industrial plant that manufactured refrigeration compressors [52]. Sheboygan River was classified as an area of concern (AOC) by the USEPA [53], 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 [52]. 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 [54]. Dredging of contaminated sediments and habitat restoration projects in Sheboygan AOC began in August 2012, and concluded in June 2013 [53,55]. 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 cleanup [55], the current levels of PCBs concentration could be lower than those estimated in this work.

Regarding human health risks, 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 [56]. According to this study, the average 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 [10]. In general, these fish would likely not come entirely from the Great Lakes. However, in order to be conservative, the risks for weekly and monthly consumers are discussed below.

The health risks due to PCBs for a weekly consumer are relatively small in Lake Huron and Lake Ontario. However, there are a couple of sites where the hazard index is higher than the considered threshold; "Saginaw River" (Lake Huron, Figure 4) for weekly consumers, and "Eighteenmile Creek" (Lake Ontario, Figure 6) for monthly consumers. On the other hand, in Lake Michigan and Lake Erie (Figures 3 and 5), for a weekly consumer the hazard index is greater than the considered threshold in most of 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 are predicted to be relatively great in both lakes.

3.3. Uncertainties and limitations of the case study

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 (obtained from [35]). This significantly reduces the uncertainty incorporated by these parameters in the results compared to factors found in bibliography that are not species-specific, such as [11]. Another source of uncertainty is the selection of the food chain. In this study it is composed by two invasive species—zebra mussel and round goby—that provide a pathway for contaminants to reach higher level predators. The high filtering capacity and bioconcentration rates of zebra mussels probably lead to overestimation of health risks, since humans also consume fish species other than smallmouth bass, and in general fish also consume organisms that bioaccumulate less amount of contaminant than mussels.

Secondly, the model computes the *LADD* for humans that consume contaminated species. Because human consumption during long periods of time (up to 60 years) is being analyzed, there is uncertainty associated with the concentration of PCBs in future years. The tool estimates the risk levels assuming the concentrations of contaminants in zebra mussel remains constant (at each site) during the exposure period. Although the concentrations should eventually decrease considering the long-term banned production of PCBs, no increasing or decreasing trends where found analyzing data from the last two decades.

Thirdly, the tool estimates cancer risk and hazard index using the *CSF* and *RfD*, respectively. On the one hand, these parameters have intrinsic uncertainties since 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. However, different PCB congeners could have different toxicity and biological activity.

It is important to highlight that the uncertainties described above are considered acceptable for a screening-level risk assessment, where minimal data is used and conservative assumptions are encouraged. The actual risks are likely to be lower than the ones estimated in this study, however, it is not possible to know how much lower. Regarding the sensitivity of the results to changes in the parameters, it can be observed that the model equations presented in Section 2.1 are linear, and moreover, the results of C_{pred}, *LADD*, cancer risk, and hazard index are proportional to the parameters used in the model. Therefore, a small increase (decrease) in the value of a parameter, for instance 10%, generates an increase (decrease) of 10% in the results if they are directly proportional (i.e., cancer risk and *CSF*), and a decrease of 9% (increase of 11%) if they are inversely proportional (i.e., hazard index and *RfD*).

In the previous paragraphs, uncertainties and limitation that are mainly related with the parameters of the model 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. 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. Although the study of the risks due to other contaminants is beyond the scope of the work, it is important to note that 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 [57]. 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 noncancer risks were exceeded in some sites only for a daily consumer during a 30-year exposure duration. In addition, trends for metal concentrations in zebra mussels were studied and, in general, it was found that the levels remained constant or had a decreasing trend in the last two decades.

4. Conclusions

4.1. Summary

In this work, a Python code with ArcMap® interface is developed to perform bioaccumulation risk analysis. The tool is named Arc-BEST, and 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 and integrates the strengths and simplicity of the BEST model with the powerful capabilities of GIS software. Arc-BEST is easy to use and increases model creation speed with respect to the original tool when several sites are being analyzed, improving the analysis, comparison, and visualization of results. Furthermore, the model was improved to consider up to four trophic levels.

Using Arc-BEST, the ecological and human health risks due to PCBs are studied in the Great Lakes region of the Midwest of the United States. PCBs are man-made organic chemicals, and are among critical contaminants in the lakes. Following a screening-level risk assessment approach, the study is meant to be conservative and use minimal data, and protective assumptions are made. The ecological hazards are addressed comparing total PCBs levels in predator species with the ecological threshold of 4 mg/kg. For 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. The highest hazard is obtained in “Sheboygan River” (Lake Michigan), where concentration in smallmouth bass reaches 17 mg/kg. 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 risks, lower and upper limits for body weight and exposure duration are considered to account for uncertainties. Moreover, the parameters that are used to estimate cancer risk and hazard index for humans (*CSF* and *RfD*) also account for uncertainties in their definition. Cancer risk and hazard index (associated with non-cancer effects) are estimated based on long-term exposure to PCBs from consumption of 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 weekly and monthly consumers. Overall, Lake Huron and Lake Ontario present the lower risks 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 not safe to consume. In Lake Michigan and Lake Erie the hazard index exceeds the threshold in most locations for a weekly consumer. However, in Lake Michigan 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 bioaccumulation of 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 identified 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, as vast areas of relatively 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.

4.2. Recommendations

Firstly, it is crucial to have 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 [32]. Regarding 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 [58]. It also uses a performance based quality assurance process to ensure data quality [43].

Secondly, it is important to define 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, the BMFs used should be 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, i.e., data of body weight, lifetime, and fish consumption. Some references used in this work that could be useful for other studies in the United States are the following: [49,50,56].

In conclusion, Arc-BEST is a useful tool for screening-level risk assessment, as it was shown 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 further collection of data, to ultimately enhance humans' health and quality of life, and protect ecosystems. When the presumption of risk cannot be rebutted under conservative assumptions, it is advisable to use a more complex bioaccumulation risk assessment and perform field studies in order to improve robustness of the results and better characterize the risk.

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Conflict of interest

The authors declare no conflict of interest.

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