Final Project Report

for

Eighteenmile Creek Area of Concern Mink Prey Survey and Oak Orchard Creek Add-on

Project GL-00E02088-1

December 1, 2021

Revised July 21, 2022

Prepared for

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Lockport, NY

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Executive Summary

1. In the Great Lakes Basin, the International Joint Commission has identified 43 Areas of Concern (AOC) where pollution from past industrial production and waste disposal practices has created hazardous waste sites or contaminated sediments. Beneficial Use Impairments (BUI) have been identified for each AOC, and for an AOC to be delisted removal of each of its BUIs must be documented.
2. The American Mink (*Neovison vison*) is the most sensitive mammal in North America to polychlorinated biphenyls (PCB), dioxins (CDD) and furans (CDF). The purpose of this project was to document whether mink consuming a diet with high proportions of aquatic prey from the Eighteenmile Creek (EMC) AOC and Oak Orchard Creek (OOC) reference area (REF) would accumulate concentrations of chemicals of concern (COC) high enough to cause chronic (health) or acute (lethal) effects in mink.
3. Mink prey tissues (amphibian, crayfish, lower [LF] and upper [UF] trophic level fish, e.g., sunfish and bass, respectively) were analyzed for total mercury (THg), total PCB and co-planar PCB, CDD and CDF, and our results compared to previous studies by Brockport (Genesee River [GR] portion of the Rochester Embayment [RE] AOC, Buffalo River [BR] AOC) and Ecology and Environment, Inc. (EMC AOC, OOC REF).
4. We also used literature-based diet (using COC concentrations in composited mink prey tissue) and bioaccumulation (using COC concentrations in water) models to predict COC concentrations in mink living in the EMC AOC and OOC REF. The two models agreed within 2.6 ±1.6 pg/g PCB TEQ for EMC, and 3.2 ± 0.6 pg/g for the OOC REF. These differences as a percent of the diet model results were 4.3 ± 3.3 % for EMC, and 94.0 ± 1.0 % for OOC REF. The percent difference between the two models was much higher in the OOC REF due to the much lower PCB TEQ concentrations there.
5. TPCB and PCB TEQ concentrations in mink prey in the EMC AOC are an order of magnitude or higher than they are in the OOC REF, GR portion of the RE AOC and BR AOC. Concentrations of THg and CDD/CDF TEQ are not of biological concern to mink in any of the four locations.
6. Removal of BUIs for the EMC AOC
    1. Based on the results of this study, BUI #3, Criterion 3, *"PCB concentrations in fish tissue are below thresholds likely to result in **acute** toxicity to fish or piscivorous wildlife (birds and **mammals**)"* can be removed for the EMC AOC. Although the concentration of TPCB in the UF prey group in the AOC exceeds the acute Lowest Observed Adverse Effect Level (LOAEC) when considered in isolation, weight-of-evidence indicates that PCBs in the AOC are not likely to cause acute toxicity in mink.

2. Based on the results of this study, BUI #5, Criteria 1 "*PCB concentrations in fish tissue from comparable functional feeding groups are similar to reference sites*" OR 2 "*PCB concentrations in fish or other prey are below tissue concentrations known to cause deformities or reproductive impairment in piscivorous wildlife*" are not recommended for removal. Concentrations of TPCB and PCB TEQ are significantly higher in the EMC AOC than the GR portion of the RE AOC, BR AOC and OOC REF (Criterion 1), and concentrations of TPCB and PCB TEQ in the AOC greatly exceed their chronic LOAECs (Criterion 2).

7. Other recommendations

   a. Getting PCB TEQ, not TPCB, below chronic LOAECs in contaminated ecosystems is the best way to protect the health of piscivorous birds and mammals. In the future, the RAP Coordinating Committee should consider using water sampling and the bioaccumulation model used in this study that was optimized for the EMC AOC to predict PCB TEQ concentrations in mink. Modeled PCB TEQ concentrations ranged by factors of 4.0 to 9.2 higher than the 9.2 pg/g chronic LOAEC relevant to BUI #5 Removal Criterion 2. Given currently high TEQ in mink prey it will take many years for predicted PCB TEQ to fall below the LOAEC, at which time another mink prey study should be conducted so that then existing COC concentrations in prey can be used in this study's diet model. If the bioaccumulation and diet models agree that PCB TEQ concentrations are less than the chronic LOAEC, BUI #5 Removal Criterion 2 would be satisfied. An alternative to the approach described above would be to locate and remediate source areas in EMC to reduce PCB concentrations in water and, subsequently, mink prey in the AOC below chronic LOAECs for mink, which would be a long and costly process.

   b. Another approach for the RAP Coordinating Committee to consider now would be to examine the findings reported in the mink habitat suitability and signs portion of this study that led the project team to decide that a mink prey study was the only way to address BUIs #3 and #5. Mink habitat suitability was low, only one definitive mink sign was observed, and the area of the AOC is so small that only 1-2 male mink at a time could hold territories there. While some mink may pass through the AOC to reach other habitats, the AOC itself cannot sustain a viable mink population and the same is true for this study's "source area" between Ide Road and Burt Dam. While any mink living long-term in the AOC would exceed the chronic LOAEC for PCB TEQ, the RAP Coordinating Committee might consider removing BUI #5, Criterion 2 on the basis that few or no mink can be long-term residents of the AOC due to habitat quality and area constraints.

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Introduction

In the Great Lakes Basin, the International Joint Commission (IJC) has identified 43 Areas of Concern (AOC) where pollution from past industrial production and waste disposal practices has created hazardous waste sites or contaminated sediments. Beneficial Use Impairments (BUI) have been identified for each AOC, and for an AOC to be delisted removal of each of its BUIs must be documented. This study assessed whether chemicals of concern (COC) could negatively impact mink populations along Eighteenmile Creek (EMC) and addressed two BUIs: *Degradation of Fish and Wildlife Populations* and *Bird or Animal Deformities or Reproductive Problems*. Criteria for removing these two BUIs in the EMC AOC are in Table 1 and definitions of acronyms used in this report are in Table 2.

EMC AOC study area

EMC and its watershed (Figure 1) are located within Niagara County, NY, approximately 18 miles east of the Niagara River. It has three major tributaries, Gulf Creek, East Branch Creek and the New York Barge (Erie) Canal, and flows north into Lake Ontario at Olcott, NY. The AOC boundary includes Olcott Harbor and extends to the farthest point at which backwater conditions exist in EMC during Lake Ontario's highest monthly average lake level. This point is located just downstream from Burt Dam, ~2 miles south of Lake Ontario. The "Creek Corridor" in the City of Lockport, NY, and the watershed south of Burt Dam are considered contaminant "source areas" (SA). This project focused on two sections of EMC: the AOC from Lake Ontario to Burt Dam and the SA between Burt Dam and Ide Road near Newfane, NY (Figure 1).

Basis for the decision to focus on mink prey

The American Mink (*Neovison vison*) is an excellent sentinel species to use in relation to BUIs 3 and 5 for the EMC AOC (Table 1) because it is highly sensitive to COCs in the environment. This is primarily due to the high trophic level (TL) of mink, and because when living in contaminated riparian areas they consume mostly aquatic animals (cf. Alexander 1977, as cited by USEPA 1993) that often contain high concentrations of COCs. Previous research has shown that mink populations are especially sensitive to dioxins (CDD), furans (CDF) and dioxin-like coplanar polychlorinated biphenyls (PCB), which at part per billion (ng/g, total PCB) or trillion (pg/g; CDD, CDF and coplanar PCB toxic equivalent [TEQ]) concentrations cause reproductive failure. Minks are especially well suited for the EMC AOC and SA study because the concentrations of total PCB and PCB TEQ are very high in EMC. Above a whole-body residue of 9.2 pg/g, these chemicals also may cause cancerous jaw lesions, the most sensitive biomarker of effect (Haynes *et al.* 2009) known for mink. Studies in the 1970s and 1980s showed that organo-chlorine pesticides failed to present significant toxicological effects for mink (Giesy *et al.* 1994). They would be even less suitable for study now because concentrations of these chemicals in the environment have decreased.

In August 2018, all muddy areas along the entire EMC shoreline between Lake Ontario and the southern extent of the Burt Dam reservoir were examined for mink footprints by an

experienced trapper and the field crew (Figure 2). Also, logs and rocks along shore were checked for mink scat and other signs (Lesmeister and Nielsen 2011, Yamaguchi and Macdonald 2003, Birks and Linn 1982). From Lake Ontario to Burt Dam, one definitive (several distinct tracks) and three faint, potential signs of mink were observed. No signs of mink were observed along the shoreline of the SA (Haynes and Wellman 2019).

In August 2018, the experienced mink trapper and field crew made observations, by boat and on foot, of potential mink habitat along the entire EMC shoreline between Lake Ontario and the southern extent of Burt Dam reservoir (Figure 2). Following the Riverine-Lacustrine Suitability Index (SIRL, Allen 1986) and the trapper's experience, mink habitat suitability scores were calculated for each of the 36 stream reaches surveyed. Both the SIRL (mean = 31%) and the trapper's (mean = 32%) scores rated mink habitat quality low in the entire study area (Haynes and Wellman 2019). Based on these results (Figure 2) and the small size of the study area, the EMC project team decided that the study area would not contain enough mink to achieve project objectives (at least 20mink needed to be trapped). Accordingly, as anticipated in the QAPP, we switched to a mink prey study that would allow us to estimate exposures of mink to total mercury (THg), PCBs and CDD/CDFs. In 2020, the project was expanded to include selected sampling in Oak Orchard Creek (OOC), which is a long-time reference area (REF) for AOC and Superfund studies, so that we could construct diet and bioaccumulation models for mink exposure to COCs in the OOC REF.

Study objectives and hypotheses

EMC AOC and SA

Objective 1: Collect potential aquatic prey species of mink and analyze them for COCs to determine whether the health of mink would be at risk if they consumed prey living in the AOC and SA. Prey tissues were analyzed for CDD/CDF and PCB congeners and THg. Potential terrestrial prey species were not collected because they are primarily herbivores that contribute very low contaminant concentrations to a mink's diet compared to aquatic prey.

Objective 2: Use COC concentrations in the available prey for EMC mink to construct a diet model to estimate consumption risks for mink, then compare model predictions and analytically determined concentrations in sampled prey to published dietary lowest observed adverse effect concentrations (chronic LOAECs).

Objective 3: Compare COC concentrations determined for mink prey in the AOC and SA to mink prey in other AOCs (Buffalo River AOC, BR AOC; Genesee River portion of the Rochester Embayment AOC, GR AOC, and the OOC REF area between the Waterport Station Dam and Lake Ontario (Figure 3).

Objective 4: Collect whole water samples (dissolved and particulate fractions) from the EMC AOC and SA and in Lake Ontario (LO) away from tributary influences in spring, summer and fall seasons. Whole water samples also were collected in the OOC REF by

the U.S. Army Corps of Engineers (USACE) in March 2021 and August 2020 and by the U.S. Environmental Protection Agency from 2005-2010 (Data provided by Andrew Lennox, USACE Buffalo District). COC concentrations in whole water samples were the foundation for bioaccumulation model used to predict chemical concentrations in mink diets in EMC AOC and SA and OOC REF.

Hypothesis 1: COC concentrations in mink prey do not differ significantly between the EMC AOC and SA.

Hypothesis 2: COC concentrations in mink prey do not differ significantly among the EMC AOC and SA, BR AOC, GR portion of RE AOC and OOC REF.

Hypothesis 3: COC concentrations in mink prey in the EMC AOC and SA, BR AOC, GR portion of RE AOC and OOC REF are not higher than published dietary LOAECs.

Hypothesis 4: COC concentrations in water from EMC AOC and SA, OOC REF and LO away from tributary influences are not significantly different.

Diet model

Objective 5: Use literature reports of mink diets (USEPA 1993) and trophic levels of their prey to construct both worst case (92% aquatic with 58% high trophic level fish, thus highest potential exposure to contaminants) and likely case (65% aquatic and 35% terrestrial) diet models, including literature-based proportions of four aquatic prey groups: amphibians (AM), crayfish (CR), and lower (LF) and upper (UF) trophic level fish.

Objective 6: Use diet models to estimate exposure of mink to COCs in the EMC AOC and SA and compare diet modeling results to published LOAECs.

Hypothesis 5: COC concentrations estimated by diet models using data for the EMC AOC and SA are not significantly different.

Hypothesis 6: COC concentrations estimated by diet models using data for the EMC AOC and SA are not higher than published dietary LOAECs.

Oak Orchard Creek reference area

OOC (Figure 3) is a reference water body (no known sources of COCs beyond background levels) used by federal and state agencies to compare with chemical and biological findings from AOC and Superfund studies. Brockport's sampling for the OOC REF included collection and analysis of COCs in CR.

Objective 7: Use COC data from a previous study (E & E 2019) for THg and PCB (total and TEQ) in LF and UF common to EMC and OOC, along with crayfish COC data collected by Brockport, to model mink diet in EMC and OOC and compare it to published LOAECs.

Hypothesis 7A: COC dietary exposure estimates for the OOC REF are not significantly different from dietary exposure estimates for EMC SA and AOC.

Hypothesis 7B: COC concentrations estimated by diet models using data for the OOC REF are not higher than published dietary LOAECs.

Bioaccumulation model

Objective 8: Modify a published bioaccumulation model (derived from Sample *et al.* 1996 by Wellman *et al.* 2009 and Wellman 2006) to reflect concentrations of PCB TEQ measured in EMC water. The resulting model will allow prediction of COC concentrations in mink diet based on concentrations in whole water, and comparison of those predicted concentrations with diet models and published LOAECs.

Objective 9: Use the bioaccumulation model developed for EMC (Objective 8) to estimate COC concentrations in mink diet from concentrations in whole water collected from the OOC REF.

Hypotheses 8-9: Predictions of the bioaccumulation models for the EMC and OOC REF will match (±20%) predictions of the EMC and OOC REF diet models.

BUI removal criteria

Objective 10: Evaluate BUI 3, *Degradation of Fish and Wildlife Populations*, removal Criterion 3, "PCB concentrations in fish tissue and other prey are below thresholds likely to result in **acute** toxicity to fish or piscivorous wildlife (birds and **mammals**)."

Objective 11: Evaluate BUI 5, *Bird or Animal Deformities or Reproductive Problems*, removal Criterion 1, "PCB concentrations in fish tissue from comparable functional feeding groups are similar to reference sites" **OR** Criterion 2, "PCB concentrations in fish or other prey are below tissue concentrations known to cause deformities or reproductive impairment in piscivorous wildlife". This study evaluated both criteria.

Hypothesis 10: PCB concentrations in fish tissue and other prey are below thresholds likely to result in acute toxicity to fish or piscivorous mammals.

Hypothesis 11A: PCB concentrations in fish tissue from comparable functional feeding groups are similar to reference sites.

Hypothesis 11B: PCB concentrations in fish or other prey are below tissue concentrations known to cause deformities or reproductive impairment in piscivorous wildlife.

Use of Toxic Equivalency Factors and Toxic Equivalents for PCBs

Observed toxic effects of PCBs are predominantly caused by interaction of coplanar PCBs (and also co-planar CDDs and CDFs) with the aryl hydrocarbon receptor (AhR, Giesy and Kannan 2002, Van den Berg *et al.* 2006) and not TPCB concentration, *per se*. Toxic effects of PCB congeners interacting with the AhR can be described by toxic equivalency factors (TEF) that quantify the relative toxic effects of co-planar COCs in terms of the effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD, TEF = 1), the most toxic co-planar COC (Van den Berg *et al.* 2006). Ortho-substituted (non-coplanar) PCBs do have adverse effects (e.g.,

neurological, hormonal), but only at very high concentrations, so they are not likely to significantly contribute to toxic effects at ecological concentrations (Giesy and Kannan 2002). Environmental weathering (including bioaccumulation) of PCBs increases proportions of coplanar PCBs in mixtures, thus weathered PCB mixtures are more toxic than their parent technical mixtures (Giesy and Kannan 2002). Because it accounts for these weathering effects and for toxicity of PCB congeners at ecological concentrations, TEQ provides a better indicator of hazard to wildlife than do TPCBs (Giesy and Kannan 2002). Hence, this study reports TEQ for PCBs and total TEQ, including coplanar CDDs/CDFs, and TPCBs.

Materials and Methods

Field sampling

From fall 2018 to fall 2020, three whole water samples were collected at three locations in the EMC AOC and SA and >1 mi. offshore in Lake Ontario away from tributary influences, one sample at each location in spring, summer and fall (Table 3). Water samples were collected in hexane-rinsed, labeled 3.8L brown glass bottles and placed on ice in coolers immediately. Upon return to the Brockport Lab, unfiltered water was refrigerated before next day, overnight shipment on wet ice to ALS Environmental, Kelso, WA, for chemical analyses of PCB, CDD and CDF congeners and THg (see table 2 for definitions of acronyms).

In suitable shallow habitat, 40-50 CR were caught by hand after flipping rocks in EMC and OOC. In EMC, 10 AM were caught with long-handled dip nets in suitable riparian habitat, and 10 LF and 5 UF were caught by boat electrofishing then placed in an aerated live well for later sorting and processing of fish to be kept for analysis or released alive. A minimum of 70 g of each prey type (1g for stable isotope analysis and 20g each for THg, PCB congener and CDD/CDF congener analyses) was collected in three sampling seasons (Table 3). Captured prey were placed in zip lock bags on ice in the field (one each for CR, AM, LF and UF).

Lab processing of samples

Within 24-48 h, prey organisms were processed in the Brockport Laboratory and frozen.

1. Specimens in each of four mink prey trophic groups collected during each sampling season were identified, measured (mm) (fish: tip of snout or lower jaw to tip of caudal fin; crayfish: tip of rostrum to tip of telson; amphibians: snout to vent), and weighed (g) with a digital top-loading scale.
2. With hexane-rinsed tools, ~1g of muscle tissue was excised from ten specimens in each trophic group (five specimens of UF), placed in labeled, hexane-rinsed glass vials, frozen, and saved to ship for stable isotope analysis by the Cornell Isotope Laboratory (COIL) in Ithaca, NY.
3. The remaining tissue (>>70g) from each trophic group for each season was placed in a labeled zip lock plastic bag, frozen and, at the end of each sampling season, shipped overnight on wet ice to Kelso, WA, for chemical analyses by ALS Environmental.

4. Code numbers were placed on or in each sample container as it was filled. With their code numbers, all data from field and lab data sheets were entered into spreadsheets and saved on two data storage devices (lab computer, Project Director's home computer) within 24 h.
5. Upon receipt, COIL and ALS Environmental froze and subsequently thawed, ground up and homogenized (ALS) or freeze dried (COIL) specimens from the prey trophic groups. At ALS, each of the three seasonal composited samples for each trophic group was split into four aliquots and frozen in labeled, hexane-rinsed glass. Tissue samples were analyzed by for THg, PCB congeners (the sum of which gave TPCB) and CDD/CDF congeners. The 12 coplanar PCB congeners and 17 CDD/CDF congeners with TEFs were used to calculate PCB TEQ and CDD/CDF TEQ, respectively. Excess tissue was frozen in reserve jars for contingencies.

Mink hazard assessment

Prey group samples

Concentrations of THg, TPCB and TEQ for CDD/CDF and coplanar PCB congeners found in mink prey were compared to published chronic and acute LOAECs. For THg, chronic and acute LOAECs are 500 ng/g and 1,000 ng/g, respectively (Dansereau *et al.* 1999). For TPCB they are 960 ng/g (Bursian *et al.* 2006) and 5,000 ng/g (Aulerich and Ringer 1977). TEQs for CDD/CDF and co-planar PCB congeners were calculated using World Health Organization TEF values from Van den Berg *et al.* 2006. TEQ was summed separately for CDD/CDF and PCB congeners, then the categories were summed to yield total TEQ for each prey group sample (Electronic Appendix A: Data analysis worksheet "EMC Prey"). For PCB/CDD/CDF TEQ, singly or combined, chronic and acute LOAECs are 9.2 pg/g (Bursian *et al.* 2006) and 1,000 pg/g (Hochstein *et al.* 1998), respectively.

Stable isotope analysis to determine mink prey trophic levels

Stable isotopes of nitrogen are used to evaluate trophic webs of ecosystems to give lifetime, integrated estimates of trophic level (TL) for organisms (DeNiro and Epstein 1978, Cabana and Rasmussen 1994). ^{14}N has a stable, heavier isotope (^{15}N) which occurs naturally, and the heavier and lighter isotopes are differentially absorbed and metabolized by organisms (Fry 1991). Usually, the lighter isotope is excreted preferentially, leading to enrichment of the heavier isotope in organisms relative to their environment or diet. This enrichment is measurable through mass spectrometry and is reported in parts per thousand (δ‰) relative to a standard: $\delta X = [\frac{R_{sample} - R_{standard}}{R_{standard}}] \times 10^3$, where X is ^{15}N and R is the corresponding ratio of ^{15}N/^{14}N. The standard for nitrogen is atmospheric nitrogen (Fry 1991).

Selective excretion of ^{14}N over ^{15}N by animals results in an increase of approximately 3.4‰ in the δ^{15}N at each trophic level; thus, ^{15}N analysis of animal tissue can determine the trophic level of the animal (Peterson and Fry 1987; Cabana and Rasmussen 1994). Muscle tissue

from each trophic group in each season were analyzed by the COIL in Ithaca, NY for isotopic ratios of $^{15}N/^{14}N$ (δN) to determine the TL of composite samples for each prey category collected in EMC and OOC (Electronic Appendix A: Data worksheet "EMC TL").

Diet Model

The diet model predicts the dietary exposure to COCs of mink in a study area by combining the COC concentrations in mink prey from that area, using a weighted average in proportions consistent with that of mink diets found in the literature. The concentration of each COC in a prey group is multiplied by that prey group's proportion of the diet, and the results are summed to yield the concentration in that diet. The model can be expressed as:

$$C_D = \sum_{i=1}^{n} C_i \times F_i \ ,$$

where C_D is the concentration of the COC in the diet, n is the number of prey categories, C_i is the concentration of the COC in prey category i, and F_i is the fraction of the diet consisting of prey category i (the sum of the fractions is 1.00).

For example, assume that a mink's diet consists of 20% terrestrial herbivores, 10% crayfish, 40% lower trophic level fish and 30% upper trophic level fish and that mean TPCB concentrations in its prey's tissues are 0 ng/g in herbivores, 10 ng/g in crayfish, 12 ng/g in lower trophic level fish and 15 ng/g in upper trophic level fish. The equation would be:

$$C_D = \left(0\frac{ng}{g} \times 0.2\right) + \left(10\frac{ng}{g} \times 0.1\right) + \left(12\frac{ng}{g} \times 0.4\right) + (15\frac{ng}{g} \times 0.3)$$

$$C_D = 0 + 1\frac{ng}{g} + 4.8\frac{ng}{g} + 4.5\frac{ng}{g} = 10.3\frac{ng}{g}$$

The mink's diet would contain 10.3 ng/g of TPCB, with herbivores contributing 0 ng/g TPCB, CR 1 ng/g, LF 4.8 ng/g, and UF 4.5 ng/g. This concentration can then be compared to LOAEC dietary concentrations.

USEPA (1993) reported the results of 17 studies of mink diet at 25 different locations where the portion of the diet from aquatic sources ranged from 13.4% to 92%. Lower (e.g., sunfish, perch) and upper (e.g., black bass, pike) trophic level fish are secondary and tertiary consumers which typically comprise 50% or more of riparian mink diets (USEPA 1993). Crayfish (omnivores) and frogs (secondary consumers) typically comprise 20% or less of riparian mink diets (USEPA 1993).

We averaged the results from the six most relevant diet studies (for mink living along rivers and streams) cited by USEPA (1993; studies averaged were Hamilton 1940, Korschgen 1958, Cowan and Reilly 1973, Alexander 1977a, b, and Burgess and Bider 1980). For each prey category, we averaged the proportion of that category from all six studies to get a "typical" proportion of the diet for that category. A "typical" riparian mink's diet consists of 33.3% UF, 13.5% LF, 10.2% crustaceans and 8.1% AM, with a total of 65% from aquatic sources.

The maximum potential dietary exposure of mink to COCs in EMC AOC water would be best represented by a study on a river in lower Michigan (Alexander 1977 cited by USEPA 1993), consisting of 57.5% UF, 27.5% LF, 4% crustaceans and 3% AM (total 92% aquatic), and 8% "other" (birds, mammals, vegetation and unidentified). We used these dietary percentages to represent a "worst-case" dietary exposure to mink of THg, co-planar PCB and CDD/CDF.

Comparison of preliminary calculations of the trophic level (see next section) of the "worst-case" diets in EMC with previous studies of the trophic level of mink in the Lower Great Lakes indicated that Alexander's diet (1977 cited by USEPA 1993) was not a good representation of mink in EMC. Studies in the Rochester Embayment AOC (Haynes *et al.* 2007) and Niagara River AOC (Haynes *et al.* 2016) measured the trophic levels of 63 trapped mink. Of those, one was at trophic level 5.13, one at trophic level 5.00, and the rest were below trophic level 5. Thus, we concluded that a more realistic "worst-case" mink diet in the EMC AOC would be at trophic level 4. To create a diet model for trophic level 4, we started with the diet proportions of the worst-case diet (Alexander 1977, cited by USEPA 1993) and, keeping the relative proportions of the aquatic prey categories constant, increased the percentage of terrestrial prey until the trophic level came down to 4.

Since we were not able to obtain amphibian samples from the EMC AOC, we had to adjust the proportions of the other prey groups to account for the missing category. For the worst-case diet scenario in the AOC, we wanted to maintain the 92% aquatic value, so we distributed the AM portion proportionally over the other three aquatic categories. For the typical diet in the AOC, we added the AM portion to the terrestrial portion of the diet, resulting in a 57% aquatic diet. We calculated diet models in the EMC SA both with and without AM.

Dietary exposures of mink in the EMC AOC and SA were estimated by multiplying the average concentration of each COC contaminant in each of the four aquatic prey groups by the corresponding portion of the modeled mink diets and summing the results. We did these calculations: 1) for the worst-case diet Alexander (1977, in USEPA 1993), 2) for the typical diet represented by the average of the six studies, and 3) for a trophic level 4 diet. Again, concentrations of individual PCB and CDD/CDF congeners were multiplied by their respective TEF, then summed to yield a total TEQ for each diet. Estimated dietary exposures were then compared to published LOAECs reported by Haynes *et al.* (2007; Electronic Appendix A: Data analysis worksheet "EMC Diet").

To compare EMC SA and AOC to OOCREF, we did a separate set of diet model calculations. In this case, we used data from CR caught in all three areas during this study along with data for pumpkinseed (*Lepomis gibbosus*, LF) and largemouth bass (*Micropterus salmoides*, UF) from E & E (2019), as these were the relevant species for which E & E had congener-specific PCB data in all three areas. We used the same diet concentrations as in the previous model for the amphibian-free typical diet (57% aquatic) and the worst-case diet (92% aquatic). This allowed direct comparison of the EMC SA and AOC to the OOC REF (Electronic Appendix A: Data analysis worksheet "OOC Comp").

Trophic level of diet

The mean trophic level for each aquatic prey group in EMC was multiplied by that prey group's proportion in the diet (the non-aquatic portion of each diet was assumed to be trophic level 1), and the results were summed to estimate the trophic levels of the model diets above (Electronic Appendix A: Data analysis worksheet "EMC Diet"). The estimated dietary trophic levels were then used in a hazard estimate by comparison with known trophic levels of mink (hence diet) determined in the RE AOC by Haynes *et al.* (2007) and the Niagara River AOC by Haynes *et al.* (2016). These trophic level estimates were also used to determine the trophic levels used in the bioaccumulation model.

Bioaccumulation Model

The bioaccumulation model, as described in Wellman *et al.* (2009), is based on Sample *et al.* (1996) and Van Gestel *et al.* (1985). Like the diet model, the bioaccumulation model also predicts the dietary exposure of mink to a persistent organic compound, which allows direct comparison of the two models. In contrast to the diet model, which uses concentrations of COCs in mink prey, the bioaccumulation model is based on each compound's total (i.e., dissolved plus particulate fractions) concentration in water, the log K_{ow} of the compound, and the trophic level of the diet. We adapted this model to estimate the dietary exposures of mink in the EMC areas to THg and PCB TEQ. We could not model bioaccumulation of TEQ from dioxins and furans because they are at least partially metabolized, an element for which this model cannot account.

The estimated dietary exposure, C_D, for each compound is found using this equation from Wellman *et al.* (2009), derived from Equation 28 in Sample *et al.* (1996):

$$C_D = \frac{C_w[100g + (177g \times P_{aq} \times BAF)]}{760g}$$

where C_w is the concentration of the congener in water, 100 g and 177 g are the daily water and food consumption rates by the mink, 760 g is the average mass of the mink (Wellman *et al.* 2009), and P_{aq} is the percent of the diet that is aquatic. Diets at trophic level 3.6 were assumed to be 65% aquatic in the SA with amphibians and 57% aquatic in both SA and AOC without amphibians. The terrestrial fraction required to force the diets to trophic level 4 varied between areas and due to presence or absence of amphibians; thus, the trophic level 4 diets ranged from 66.8% to 70.9% aquatic.

The Bioaccumulation Factor (BAF) for each compound at each trophic level is the product of the bioconcentration factor (BCF) and the Food Chain Multiplier (FCM). Given the log K_{ow} of each compound, the BCF can be calculated using a linear equation: log BCF = a log K_{ow} – b (Van Gestel *et al.* 1985, Sample *et al.* 1996).

Tables of FCM are found in Sample *et al.* (1996) and USEPA (2003, 2012a, and 2016). The calculations by USEPA (2003) are based on the model in Gobas (1993) describing the Lake

Ontario food web. USEPA (2016) uses the same values. These values are slightly lower than those found in Sample *et al.* (1996) and in USEPA (2012a). Since USEPA (2003) states that more pelagic-based food webs will have lower FCMs than more benthic-based webs, we used the values from Sample *et al.* (1996) and USEPA (2012a) as a better representation of the EMC ecosystem. As FCMs are provided, in all sources, for only one decimal place in the log K_{ow}, and only for integer TLs from 2 to 4, we interpolated to get the FCM for each compound, and for trophic levels between 3 and 4 (Electronic Appendix A: Data analysis worksheets "FCMs" and "H_2O BA"). Once the bioaccumulated concentration C_D was determined for each PCB congener, the TEQ for each was calculated by multiplying that concentration by the TEF (Van den Berg *et al.* 2006). Finally, the bioaccumulated TEQs were summed for all coplanar congeners to yield an estimate of TEQ from PCBs in the minks' diet. This was done for each trophic level of interest (Electronic Appendix A: Data analysis worksheet "H_2O BA").

To match the Bioaccumulation Model to the Diet Model results, we had to select values for *a* (slope) and *b* (intercept) in the linear equation: log BCF = *a* log K_{ow} + *b* (Van Gestel *et al.* 1985, Sample *et al.* 1996). We compared the TEQ from PCBs for each case (described by location and trophic level) in the bioaccumulation model to the TEQ from PCBs in the diet model for the same case. In selecting *a* and *b*, we chose to minimize the root sum of squares (RSS) of the differences between the two models' TEQs in the EMC SA and AOC for the typical diet and the (amphibian-free) TL = 4 diet. RSS was used so that differences with opposite signs would not cancel each other in the optimization measure; it also tends to keep all the differences close to the same size, thus optimizing equally for all included data points.

Van Gestel *et al.* (1985) reported the results of twelve studies done from 1974 to 1983 in which values for *a* ranged from 0.542 to 1.53 and values for *b* ranged from -3.03 to 0.7285. They concluded that the most reliable equation in their study was that from Veith and Kosian (1983, cited by Van Gestel *et al.* 1985), which used 122 chemicals with a large range of K_{ow}s. Thus, Van Gestel *et al.* (1985) recommended the values of *a* = 0.79 and *b* = -0.40.

Using an Excel macro (written by J. Wellman, 2021), we created a table showing the Root Sum of Squares (RSS) values for combinations of *a* and *b* in these ranges. This resulted in a diagonal "trench" of minima extending from *a* = 1.05, *b* = -2.9 to *a* = 0.5, *b* = 0.8. There was little meaningful difference between the local minima at either end of the table within these ranges. We decided to keep Van Gestel *et al.*'s (1985) recommended value for the slope a = 0.79 and find the value for the intercept b that would minimize the RSS and thus best match the diet model results (Electronic Appendix A: Data analysis worksheet "BA Macro").

We chose to match the EMC bioaccumulation model to the EMC diet model based on our composited samples, not including any E & E (2019) samples, because we could better represent the mink diet in EMC by including more species of fish, and we wanted to avoid any potential errors due to conversion of E & E's fillet concentrations to whole fish concentrations. We then used this bioaccumulation model, optimized for EMC using our samples, to predict PCB TEQ in OOC REF. However, for that comparison with the OOC REF bioaccumulation model,

we had only the OOC REF diet model based on E & E (2019) data that required conversion of fillet to whole fish concentrations (Skinner *et al.* 2009).

Data comparability and statistical analyses used

Statistical comparisons among locations for which we had equivalent data for this and historical (E & E 2019; Haynes and Wellman 2015 a, b) studies were made for non-lipid-adjusted concentrations of total mercury (THg), total PCB (TPCB), PCB TEQ and CDD/CDF TEQ. No lipid adjustments were made because in the wild mink consume most soft tissues of their prey (perhaps not the gall bladder). For TEQ we focused on PCBs because they alone exceeded mink dietary LOAECS in EMC, whereas CDD/CDF TEQ comprised only 5.1 ± 4.6% of total TEQ across this study and did not cause any LOAECs to be exceeded when added to PCB TEQ.

Composited samples of crayfish and lower trophic level fish (mostly pumpkinseed and bluegill) were analyzed for THg, TPCB and PCB TEQ in this and historical studies (E & E 2019; Haynes and Wellman 2015 a, b), but not upper TL fish. Brockport analyzed composited samples of upper TL fish and E & E analyzed skin-on fillets of individual upper TL fish, in both cases northern pike (*Esox lucius*) and largemouth bass. To address the difference among composited samples and individual fillets of fish, we constructed composited samples of E & E individual fillets, consisting of one pike and three bass, then calculated the mean concentration of the four fillets in each new composited "sample." Based on fillet data published by Skinner *et al.* (2009), we multiplied mean composited fillet concentrations by 2.8 (conversion factor for largemouth bass) to estimate mean whole-body concentration for each constructed composited sample. The reasonableness of this approach depends on three assumptions:

1. Weights of composited fish were similar across Brockport and E & E samples. Because we did not record and E & E (2019) did not report weights of individual UF fish, we could not apply the formula used by Skinner *et al.* (2009) to convert COC concentrations in individual fish fillets to concentrations in individual whole fish.
2. Conversion factor (2.8 for largemouth bass; Skinner *et al.* 2009) from fillet concentration to whole body is similar for northern pike (for which no conversion factor was provided by Skinner *et al*.) and smallmouth bass that were included in some Brockport UF composited samples.
3. Taking the constructed composite sample approach for statistical comparisons of COC concentrations among the five locations where UF fish have been collected by Brockport and E & E (2019) is better than comparing composited to individual fillet samples.

Because treatment data were not normally distributed with equal variance, non-parametric statistics were used. The Wilcoxon Rank Sum Test (WRS) was used for two-sample tests and Kruskal-Wallis AOV of Ranks (KW) was used for three or more sample tests ($\alpha = 0.05$) of null hypotheses (Statistix 2013). When a KW test was significant, Dunn's All Pairwise Comparison test (DAPC) was used to distinguish significant differences among treatments. All statistical analysis results are in Electronic Appendix B.

Results

Species composition and trophic levels of potential mink prey collected in this study

One species of CR, the northern clearwater crayfish (*Orconectes propinquus*), was collected in the EMC SA and AOC and in the OOC REF. No AM, LF and UF were collected during this study in the OOC REF. Three AM species were collected in the EMC SA: green frog, (*Lithobates* [formerly *Rana*] *clamitans*), leopard frog, (*L. pipiens*) and American toad (*Anaxyrus americana*). Only two American toads were observed in the EMC AOC, so no chemical data for amphibians could be obtained. LF species included in each composited sample were mostly bluegill (*Lepomis macrochirus*), pumpkinseed and a few yellow perch (*Perca flavescens*), UF in each composited sample was mostly largemouth and smallmouth (*Micropterus dolomieu*) bass and one northern pike (Table 4; see Table 2 for acronym definitions).

In the EMC AOC, TL (standard deviation), was 3.98 (0.06) for CR, 4.82 (0.21), for LF and 5.14 (0.27) UF) (Table 5). In the EMC SA, trophic level was 2.50 (0.13) for AM), 3.80 (0.21) for CR, 4.43 (0.11) for LF, and 5.20 (0.06) for UF (Table 5). Only crayfish were collected in OOC, and their trophic level was 4.37 (0.06). When AOC and SA TLs were averaged, there were statistically significant differences in trophic levels of the four mink prey groups (KW: $p < 0.0001$; DAPC: UF > CR & AM; LF = AM, CR & UL) (Electronic Appendix B, worksheet "Brkprt Mink Prey Results").

BUI contaminant concentrations in the tissue of likely mink prey in EMC AOC and SA and OOC REF

Amphibian tissue did not exceed dietary LOAECs for mink for any COC (Table 5). See Electronic Appendix B, worksheet "Brkprt Mink Prey Results" for the statistical data and calculations that provided the results reported in this section.

Total Mercury

For CR, concentrations of THg did not differ significantly among the EMC AOC (35.8 [38.3] ng/g), SA (30.2 [26.0] ng/g), and OOC REF (13.5 [2.7] ng/g) (KW: $p = 0.6262$). Brockport did not collect fish in OOC. For LF (WRS: $p = 1.000$) and UF (WRS: $p = 1.000$), THg also did not differ significantly between EMC AOC and SA (Table 5). CR, LF and UF did not exceed the acute (1,000 ng/g) or chronic (500 ng/g) dietary LOAEC for THg (Dansereau *et al.* 1999). UF, with the highest concentration of THg, was less than half the chronic LOAEC (Electronic Appendix A, worksheet "EMC Prey").

Total PCB

Concentrations of TPCB for CR in the SA (1,210 [1,413] ng/g) exceeded concentrations in the OOC REF (7.7 [3.7] ng/g) but not in the AOC (293 [170] ng/g) (KW: 0.0067; DAPC: EMC SA > OOC REF; EMC AOC = EMC SA & OOC REF). TPCB in CR in the SA exceeded the chronic LOAEC (960 ng/g; Bursian *et al.* 2006), but not in the AOC. Despite the large difference in mean TPCB, the concentrations in LF in the SA (2,307 [950] ng/g) were not statistically greater than in the AOC (619 [534] ng/g) (WRS: $p = 0.2$). The concentration of TPCB in LF was greater in the EMC SA than the chronic LOAEC (960 ng/g) but less than the acute LOAEC of 5,000 ng/g (Aulerich and Ringer

1977). For UF there was no statistically significant difference in TPCB concentrations between the SA (3,830 [468] pg/g) and AOC (6,395 [4,977] pg/g) (WRS: p = 0.7). Tissue concentrations of UF in the SA were greater than the acute LOAEC (5,000 ng/g), but not in the AOC, for TPCB. (Table 5; Electronic Appendix A, worksheet "EMC Prey").

PCB TEQ

Concentrations of PCB TEQ for CR in the SA (10.4 [8.6] pg/g) exceeded concentrations in the OOC REF (0.3 [0.02] pg/g) but not in the AOC (5.2 [6.7] pg/g) (KW: 0.0155; DAPC: SA > OOC REF, AOC = SA & OOC REF). CR PCB TEQ concentration in the SA was slightly higher than the chronic LOAEC (9.2 pg/g, Bursian *et al.* 2006). For LF, the PCB TEQ concentration in the SA (57 [44] pg/g) was not significantly greater than in the AOC (12 [16] pg/g) (KW: 0.2; AOC = SA), but the concentrations in both the SA and AOC were greater than the chronic LOAEC. For UF, there was no significant difference in PCB TEQ between the SA (165 [118] pg/g) and the AOC (137 [159] pg/g) (WRS: p = 1.0; AOC = SA), and both were much higher than the chronic LOAEC. None of the prey group samples exceeded the acute LOAEC for PCB TEQ (1,000 pg/g; Hochstein *et al.* 1998). (Table 5; Electronic Appendix A, worksheet "EMC Prey"). PCB #126, the congener with the highest TEF (0.1), was responsible for 86.1% of the TEQ across all samples (AM, CR, LF, UF; Appendix C2).

CDD/CDF TEQ

For CR concentrations of CDD/CDF TEQ were all $\leq$ 0.7 pg/g and did not differ significantly among the AOC, SA, and OOC REF (KW: p = 0.7). For LF, CDD/CDF TEQ in the SA (1.8 [2.0] pg/g) also did not differ significantly from the AOC (0.7 [0.6] pg/g) (WRS: p = 0.1). The same was true in the SA (2.3 [0.6] pg/g and in the AOC (3.4 [2.1] pg/g) for UF. Concentrations of CDD/CDF TEQ for AM, CR, LF and UF were well below the chronic dietary LOAEC for CDD/CDF TEQ (9.2 pg/g, Bursian *et al.* 2006; Table 5; Electronic Appendix A, worksheet "EMC Prey").

Total TEQ

Total TEQ was calculated by summing PCB and CDD/CDF TEQ. Concentrations of TTEQ for CR in the SA (11.0 [8.3] pg/g) exceeded concentrations in the OOC REF (0.4 [0.06] pg/g) but not in the AOC (5.9 [6.8] pg/g) (KW: 0.0155; DAPC: SA > OOC REF, AOC = SA & OOC REF). CR PCB TEQ concentration in the SA was slightly higher than the chronic LOAEC (9.2 pg/g, Bursian *et al.* 2006). For LF, TTEQ concentration in the SA (59 [44] pg/g) was not significantly greater than in the AOC (12.9 [16.0] pg/g) (KW: 0.2), but the concentrations in both the SA and AOC were greater than the chronic LOAEC. For UF, there was no significant difference in TTEQ between the SA (165 [118] pg/g) and the AOC (137 [159] pg/g) (WRS: p = 1.0), and both were much higher than the chronic LOAEC. None of the prey group samples exceeded the acute LOAEC for TTEQ (1,000 pg/g; Hochstein *et al.* 1998); Table 5). PCB TEQ accounted for 91.8 % of TTEQ (Appendix C2; Electronic Appendix B, worksheet "Brkprt Mink Prey Results"), and adding CDD/CDF TEQ to PCB TEQ did not cause further exceedances of the chronic dietary PCB/CDD/CDF TEQ LOAEC (Table 5; Electronic Appendix A, worksheet "EMC Prey").

Comparing Brockport (2013-14, 2018-20) and E & E (2019) results

Brockport collected COC concentration data (THg, TPCB, PCB TEQ, CDD/CDF TEQ; Haynes and Wellman 2015 a, b and this study) from mink prey (AM, CR, LF, UF). Ecology & Environment (E & E 2019) also collected COC concentration data (THg, TPCB and PCB TEQ) from mink prey (CR, LF and UF but not AM). Results from Brockport studies of mink prey in the EMC AOC and SA, the OOC REF (CR only), the Genesee River (GR) portion of the Rochester Embayment (RE) AOC and the Buffalo River (BR) AOC (Haynes and Wellman 2015 a, b) and E & E (2019) studies of mink prey in the EMC AOC and SA and OOC REF area were combined and analyzed to compare COC concentrations in the five areas studied by either or both Brockport and E & E (Table 6). See Electronic Appendix B, worksheet "E & E-Brkprt Mink Prey Results" for the statistical data and calculations that provided the results reported in this section.

Total Mercury

AM were collected only by Brockport in the GR portion of the RE AOC (74 [11] ng/g) and EMC SA (130 [105] ng/g), and there was no significant difference in THg concentration (ng/g) between the two areas (WRS: p = 1.0). Crayfish (ng/g) were found in the EMC AOC (35.8 [38.2]), EMC SA (30.2 [26.0]), OOC REF (13.5 [2.7]) and GR portion of the RE AOC (114.7 [16.9]), but not in the BR AOC. There were significant differences in concentrations among the four areas (KW: 0.0398; DAPC: GR AOC > EMC AOC = EMC SA > OOC REF). Concentrations of THg (ng/g) in LF differed significantly among the five areas (EMC AOC, 25.8 [20.1]; EMC SA, 26.5 [22.4]; OOC REF, 20.5 [2.1]; GR AOC, 272 [26]; BR AOC, 84.4 [8.9]) (KW: p = 0.0007; DAPC: GR AOC > BR AOC, EMC SA, EMC AOC & OOC REF). Concentrations of THg (ng/g) in UF did not differ significantly across studies (KW: p = 0.1718). Except for UF fish in the GR portion of the RE AOC (567 [44] ng/g) that slightly exceeded the 500 ng/g chronic LOAEC for THg, all TLs in the Brockport and E & E studies were below the chronic LOAEC for THg (Table 6).

Total PCB

Concentrations of TCPB in AM did not differ significantly between the GR portion of the RE AOC (4.8 [1.2] ng/g) and EMC SA (107 [28] ng/g) (WRS: p = 0.2). Concentrations (ng/g) of TPCB in the combined CR samples collected by Brockport and E & E differed significantly among the four areas sampled (EMC AOC, 489 [293]; EMC SA, 835 [975]; OOC REF, 7.9 [3.8]; GR AOC, 23.9 [4.5]) (KW: p < 0.0001; DAPC: EMC SA = EMC AOC > GR AOC = OOC REF). AM and CR did not exceed the 960 ng/g chronic LOAEC for TPCB. Concentrations (ng/g) of TPCB in LF (EMC AOC, 1,752 [623]; EMC SA. 2,902 [1084]; OOC REF, 714 [78]; GR AOC, 88 [16]; BR AOC, 381 [248]) differed significantly among areas (KW: p < 0.0001; DAPC: EMC SA = EMC AOC > BR AOC, GR AOC & OOC REF). LF exceeded the 960 ng/g chronic LOAEC for TPCB in the EMC AOC and SA. Concentrations (ng/g) of TPCB in UF (EMC AOC, 6,219 [3,382]; EMC SA, 6,911 [4,184]; OOC REF, 502 [157]; GR AOC, 332 [33]; BR AOC, 993 [184]) also differed significantly among areas for UF (KW: p = 0.0001; DAPC: EMC SA = EMC AOC > BR AOC, OOCREF & GR AOC). UF in the BR AOC slightly exceeded the chronic TPCB LOAEC and UF in the EMC AOC and SA exceeded the acute LOAEC (5,000 ng/g) for TPCB (Table 6).

PCB TEQ

Concentrations of PCB TEQ in AM did not differ significantly between the GR portion of the RE AOC (0.2 [0.3] pg/g) and EMC SA (7.2 [7.1] pg/g) (WRS: p = 0.2). Concentrations of PCB TEQ (pg/g) in the CR samples collected by Brockport and E & E (EMC AOC, 5.2 [6.7]; EMC SA, 10.4 [8.6]; OOC REF; 0.3 [0.02]; GR AOC, 0.2 [0.2]) differed significantly among the four areas (KW: p = 0.0038; DAPC: EMC SA = EMC AOC > GR AOC = OOC REF). Crayfish in the EMC SA slightly exceeded the chronic 9.2 pg/g LOAEC for PCB TEQ. Concentrations of PCB TEQ (pg/g) in LF (EMC AOC, 12.0 [10.0]; EMC SA, 44.8 [28.2]; OOC REF, 0.8 [n=1]; GR AOC, 3.3 [5.4]; BR AOC, 0.4 [0.2]) differed significantly (KW: p = 0.0002; DAPC: EMC SA = EMC AOC > BR AOC, OOC REF & GR AOC). Concentrations of PCB TEQ (pg/g) in UF (EMC AOC, 373 [312]; EMC SA, 446 [355]; OOC REF, 8.6 [0.5]; 0.8 [0.3]; BR AOC, 6.1 [3.3]) also differed significantly among areas (KW: p = 0.0002; DAPC: EMC SA = EMC AOC > OOC REF, BR AOC & GR AOC). LF and UF exceeded the chronic 9.2 pg/g LOAEC for PCB TEQ in the EMC SA and AOC. None of the samples approached the 1,000 pg/g acute LOAEC for PCB TEQ (Table 6).

BUI contaminant concentrations in water

Brockport collected whole water samples in spring, summer and fall in the EMC AOC and SA and once each season at three different locations in Lake Ontario. Concentrations (pg/mL) of THg (EMC AOC, 1.1 [1.2]; EMC SA, 1,8 [1.1]; LO, 1.3 [0.7]) did not differ significantly (KW: p = 0.5824). Concentrations (pg/mL) of TPCB (EMC AOC, 35.4 [7.2]; EMC SA, 66.8 [6.6]; LO, 0.3 [0.2]) were significantly different (KW: p = 0.0010; DAPC: EMC SA = AOC > LO). Concentrations (fg/mL) of PCB TEQ (EMC AOC, 0.16 [0.03]; EMC SA, 0.17 [0.15]; LO, 0.07 [0.07]) did not differ significantly (KW: p = 0.1016). Concentrations (fg/mL) of CDD/CDF TEQ (EMC AOC, 0.54 [0.31]; EMC SA, 0.37 [0.25]; LO, 0.48 [0.41]) also did not differ significantly (KW: p = 0.7615) among the three water bodies (Table 7; Electronic Appendix A: worksheet “Water Results”; Electronic Appendix B: worksheet “H_2O Data”).

Whole water sample data collected by the USACE in 2020-2021 and USEPA from 2005-2010 in the EMC AOC and OOC REF were analyzed for TPCB together with Brockport whole water data from EMC AOC and LO collected in 2019-2021. Concentrations (pg/mL) of TPCB in EMC AOC water (47.4 [10.3]) were significantly higher than both OOC REF (0.3 [0.1]) and LO (0.3 [0.2]) waters (KW: p < 0.0001; DAPC: EMC AOC > LO & OOC REF) (Table 7; Electronic Appendix B: worksheet “Water Results”).

Diet models

The COC concentrations found in, as well as the TLs of, prey group samples were used in diet models, which combined concentrations and TL in a proportional manner to mimic literature reports of mink diets. The diet models thus estimated mink dietary exposures to COCs found in their prey in EMC and OOC.

In the EMC SA, the typical diet including amphibians was 65% aquatic with a TL of 3.6, while the worst-case diet including amphibians was 92% aquatic with a TL of 4.6. When the

amphibians were removed from the SA diets, the typical diet was 57% aquatic with a TL of 3.6, while the worst-case diet remained at 92% aquatic with a TL of 4.7 (Table 8). As there were no amphibians in the EMC AOC, the typical diet was 57% aquatic and had a TL of 3.6, while the worst-case diet at 92% aquatic had a TL of 4.8 (Table 8).

Modeling results suggested no differences in potential dietary exposures of mink between the EMC AOC and SA (Table 8). No EMC diet models exceeded the chronic dietary LOAEC for THg (500 pg/g, Dansereau *et al.* 1999). EMC diet models for TPCB (57% and 92% aquatic) in the AOC and SA exceeded the chronic dietary LOAEC (960 ng/g, Bursian *et al.* 2006) but not the acute LOAEC (5,000 ng/g; Aulerich and Ringer 1977). All EMC diet models for PCB TEQ exceeded the chronic dietary LOAEC (9.2 pg/g, Bursian *et al.* 2006), but not the acute LOAEC (1,000 pg/g; Hochstein et al. 1998).

Diet modeling results indicated that the OOC REF had much lower potential dietary exposures for mink than the EMC AOC and SA (Table 9). None of the OOC results exceeded the chronic dietary LOAEC for THg (500 ng/g). Diet model predictions for the OOC REF were far below chronic LOAECs for TPCB and PCB TEQ. No data are known for CDD/CDF in the OOC REF. We could not calculate the TLs for OOC REF diets because we did not have TL data for the E & E (2019) fish used in this model.

Bioaccumulation models

The bioaccumulation model estimates the dietary exposure of mink to chemicals of concern based on those chemicals' concentrations in water. With the slope value a = 0.79 as recommended by Van Gestel *et al.* (1985), the minimum RSS (6.53) of the differences between the models was found at intercept b = -1.11, yielding the equation log BCF = 0.79 log Kow – 1.11 (Electronic Appendix A: Data analysis worksheet "BA Macro"). Using this equation and FCMs from Sample *et al.* (1996) and USEPA (2012a), the bioaccumulation model optimized for EMC matched the predictions of the diet model within less than 5% for typical (TL = 3.6) and TL 4 diets in EMC (Table 10). There was very close agreement of PCB congener (Figure 5) and PCB TEQ (Figure 6) concentrations predicted by the diet model and the bioaccumulation models.

Using the parameters of the bioaccumulation model as optimized for EMC, the bioaccumulation model for the OOC REF matched the OOC diet model for typical (TL = 3.6) and TL 4 diets with a mean difference of 3.2 (0.6) pg/g TEQ, just over one-third of the 9.2 pg/g chronic LOAEC, although the percent difference was much higher (94.0 [1.0] %) due to the much lower PCB TEQ concentrations in the OOC REF (Table 10).

Discussion

The overarching conclusion from the field data presented above is that, regardless of the statistical results somewhat blurred by small sample sizes, the potential biological harm to mink from concentrations of TPCB and PCB TEQ in mink prey and water in the EMC AOC and SA are an order of magnitude or greater than they are in the OOC REF, GR portion of the RE AOC

and BR AOC (Tables 5, 6 and 7). Concentrations of THg and CDD/CDF TEQ are not of biological concern to mink living in any of the five locations compared in this study.

Potential sources of error

Diet model

The diet model combines the concentrations of chemicals found in prey group samples, by incorporating them in proportions matching those of mink diets reported in the literature, to estimate the dietary exposure of mink living in areas where those prey samples were taken. The only inputs to the diet model are the COC concentrations in prey groups and the fractions of mink diet they comprise. Hence, one source of error is the uncertainty in measuring COC concentrations in prey samples, but these errors are reduced by the fractions by which they are multiplied in the diet model. Another source of error is the variation between the diet model description of mink diet based on literature values (USEPA 1993) and field conditions for mink. We have no way to quantify this potential error, but we have bounded the problem by exploring typical- and worst-case diets, with and without amphibians.

A final source of error in the OOC REF diet model (Table 9) came from using a 2.8 multiplier to convert E & E (2019) skin-on fillet concentrations for largemouth bass (Skinner et al. 2009) and northern pike (no factor provided by Skinner et al. 2009) to whole body concentrations for the same fish. Then we created composited samples of E & E fish (northern pike and largemouth bass) to match Brockport's composited samples collected in the EMC AOC and SA. Because E & E UF were collected only in the fall of 2018, while Brockport UF were collected once each in fall, spring and summer from 2018-2019, there is no way to know whether the fish sampled by the two groups were comparable in size, lipid content and, thus COC concentrations. The effect of these differences between Brockport and E & E fish samples can be seen by comparing EMC diet models in Tables 8 and 9, which show the results of using Brockport and E & E (2019) fish, respectively. Nevertheless, UF TPCB concentrations in the OOC REF (E & E fish only) were more than 10X lower than in the EMC AOC and SA (Table 6), as expected. However, this was not the case for PCB TEQ: While more than 10X lower than the concentrations in UF in the EMC AOC and SA, PCB TEQ was almost 3X higher in UF in the OOC REF than the chronic LOAEC (9.2 pg/g). We attribute the different results between TPCB (n = 6 composited samples) and PCB TEQ (n = 2 composited samples) to luck of the draw in larger vs. smaller sample sizes (Table 6).

Bioaccumulation model

Potential sources of error in the bioaccumulation model include uncertainties in values for K_{ow} and FCM, interpolations required to determine non-integer FCMs and BCFs, and non-linearity of the relationship between log K_{ow} and log BCF.

We used log K_{ow}s that were derived by computing averages across up to six values per PCB congener based on data from six different studies or models (Eisler and Belisle 1996, Hawker and Connell 1998, Jäntschi and Bolboacă 2006, Paasivirta and Sinkkonen 2009, and two

models from USEPA 2012b). The values for log K_{ow} of coplanar PCBs in those studies varied substantially; PCB 81 had the smallest log K_{ow} range (0.565) while PCB 189 log K_{ow} had the largest range (0.911). Because log K_{ow} is in the exponent of the equation $BCF = 10^{(0.79*logK_{ow}-1.06)}$, small changes in log K_{ow} create large changes in BCF and hence in BAF ($= BCF * FCM$).

We found two different sets of food chain multipliers provided by EPA (2003, 2012a, 2016), along with the explanation that FCMs vary between ecosystems (EPA 2003, Arnot and Gobas 2006). Sources of variation include characteristics of individual organisms (lipid content, diet, size, age, gender, reproductive status), species (trophic level, dietary preference, metabolic abilities) and ecosystems (temperature, water column depth, interaction of benthic species with sediment) (Arnot and Gobas 2006). We chose the available set of FCMs more likely to describe the EMC and OOC ecosystems, but without a separate study to determine the FCMs in EMC and the OOC REF, that description cannot be exact.

USEPA (2012a, 2016) recommend linear interpolation of FCMs within trophic levels, which we also had to do between trophic levels to compare with our diet model trophic levels. Linear interpolation between log K_{ow}s slightly underestimates the FCMs, as those curves are convex upward in the range of log K_{ow}s for coplanar PCBs. Differences between linear interpolations and convex cures were assumed to be negligible based on EPA's (2012a, 2016) recommendation. Linear interpolation between trophic levels also slightly underestimates the BAFs, as a best-fit curve to the FCMs of the three trophic levels for any one K_{ow} is also convex upward in the same range. The magnitude of the underestimation in the interpolation between trophic levels is shown in Figure 4 for the two PCBs with the highest toxicities, PCB 126 (log K_{ow} = 6.8) and PCB 169 (log K_{ow} = 7.4) and is also assumed to be negligible.

Arnot and Gobas (2006) did regressions to find slope, a, and intercept, b, from 392 published studies and database sources. They found that the values varied between trophic levels, i.e., autotrophs, invertebrates, and fish (trophic levels unspecified) and each had their own equations. Sources of variation are much the same as for FCMs above (Arnot and Gobas 2006), so different ecosystems will also have different equations. This finding is consistent with Van Gestel et al.'s (1985) review of ten studies all with different slopes (a) and intercepts (b), although those studies appear to be lab experiments rather than ecosystem studies.

Arnot and Gobas (2003, 2004, 2006) present a much more complex bioaccumulation model than the one used in this study that accounts for many of the sources of variation mentioned above along with others such as gill uptake and elimination, dietary uptake, fecal elimination, growth dilution, and metabolism of chemicals. They described the relationship between log BAF and log K_{ow} as "parabolic;" in their figures it is convex up with a peak at about log K_{ow} = 7.5 (Arnot & Gobas 2003). Within the range of log K_{ow} for coplanar PCBs, where 6 < log K_{ow} < 8, the slope of the curve decreases to zero, then becomes negative because the chemicals are becoming more strongly bound to DOC and POC and thus less bioavailable to the food web

(Arnot and Gobas 2003). While their model is probably more accurate, it applies to only one trophic level and requires input data that we did not have.

Our diet and bioaccumulation models show that absolute PCB TEQ concentrations are smaller in the OOC REF than in the EMC AOC and SA models by nearly two orders of magnitude (Table 10). Although we cannot quantify the errors that might occur in our bioaccumulation model, it matches the results of the diet model very well in the EMC SA and AOC. While the differences between the two models have very similar absolute size, the percent differences in OOC REF are proportionally much larger (94%) than in the EMC (4.3%); this occurs because the diet model results are much smaller in the OOC REF than in EMC AOC or SA.

Overall, these results indicate that our choices of K_{ow}s, FCMs, and *a* and *b* seem to be appropriate for the EMC and OOC REF ecosystems. *This would allow the bioaccumulation model to be used in the future as a surrogate for sampling prey, at least until the modeling results indicate that the concentrations of COCs are approaching their LOAECs, at which point another prey study could be done.*

Answers to the 12 hypotheses tested in this study

EMC AOC and SA null hypotheses

Hypothesis 1: *COC concentrations in mink prey do not differ significantly between the EMC AOC and SA*. This null hypothesis was confirmed (Table 5).

Hypothesis 2: *COC concentrations in mink prey do not differ significantly among the EMC AOC and SA, BR AOC, GR portion of RE AOC and OOC REF*. For TPCB and PCB TEQ, the EMC AOC and SA have significantly higher concentrations than the OOC REF, GR portion of the RE AOC and BR AOC. For THg, the GR portion of the RE AOC has a significantly higher concentration than the other four study sites (Table 6).

Hypothesis 3: *COC concentrations in mink prey in the EMC AOC and SA, BR AOC, GR portion of RE AOC and OOC REF are not higher than published dietary LOAECs*. THg concentrations in mink prey were below the chronic 500 ng/g chronic LOAEC in all areas except for a small exceedance by UF in the GR portion of the RE AOC. TPCB and PCB TEQ concentrations in crayfish and amphibians were below their chronic LOAECs of 960 ng/g and 9.2 pg/g, respectively, except for PCB TEQ in CR in the EMC SA that slightly exceeded the chronic LOAEC. In LF, TPCB and PCB TEQ concentrations were considerably higher than their chronic LOAECs in the EMC AOC and SA (960 ng/g and 9.2 pg/g, respectively) and well below their chronic LOAECs in the OOC REF, BR AOC and GR portion of the RE AOC. In UF, TPCB exceeded its acute LOAEC (5,000 mg/g for Arochlor 1254) in the EMC AOC and SA while TPCB in the BR AOC slightly exceeded the chronic 960 ng/g LOAEC. TPCB concentrations in the GR portion of the RE AOC and OOC REF were far lower than the chronic LOAEC. PCB TEQ exceeded the chronic LOAEC considerably in the EMC AOC and SA but not in the BR AOC and GR portion of the RE AOC. A three-fold exceedance of the chronic PCB TEQ LOAEC in the OOC REF is best

explained by small sample size (see footnote in Table 6). CDD/CDF TEQ was below its chronic LOAEC of 9.2 pg/g at all locations and contributed only 5.5 ± 4.3% to total TEQ. TPCB and PCB TEQ are by far the major COCs posing risk to mink in EMC (Table 6).

Hypothesis 4: *COC concentrations in water from EMC AOC and SA, OOC REF and LO away from tributary influences are not significantly different*. For Brockport data alone, concentrations of TPCB in the EMC AOC and SA were greater than in LO, while concentrations of THg, PCB TEQ and CDD/CDF TEQ did not differ among the three water bodies (Table 7). Using Brockport, USACE and USEPA data, TPCB concentrations in the EMC AOC were greater than in the OOC REF (Table 7).

Diet Model null hypotheses

Hypothesis 5: *COC concentrations estimated by diet models using data from the EMC AOC and SA are not significantly different*. The diet model suggested no differences in predicted dietary exposures between the EMC AOC and SA (Table 8).

Hypothesis 6: *COC concentrations estimated by diet models using data from the EMC AOC and SA are not higher than published dietary LOAECs*. No diet model predictions for EMC SA and AOC exceeded the chronic LOAEC for THg (500 ng/g). For TPCB, all diet model predictions exceeded the chronic dietary LOAEC (960 ng/g.), but none exceeded the acute dietary LOAEC (5,000 ng/g for Arochlor 1254). For PCB TEQ, all diet models exceeded the chronic dietary LOAEC (9.2 pg/g) by at least a factor of five. None of the diet models exceeded the acute dietary LOAEC for TTEQ (1,000 pg/g).

Oak Orchard Creek null hypotheses

Hypothesis 7A: *COC dietary exposure estimates for the OOC REF are not significantly different from dietary exposure estimates for the EMC SA and AOC*. The OOC REF had much lower modeled predicted dietary exposures than the EMC AOC and SA for THg, TPCB and PCB TEQ (Table 9).

Hypothesis 7B: *COC concentrations estimated by diet models using data from the OOC REF are not higher than published dietary LOAECs*. Dietary exposures of COCs in OOC REF were well below chronic LOAECs for THg, TPCB and PCB TEQ.

Bioaccumulation model null hypotheses

Hypotheses 8-9: *Predictions of the bioaccumulation models for the EMC and OOC REF will match (±20%) predictions of the EMC and OOC REF diet models*. Five diet and bioaccumulation models of PCB TEQ with different trophic levels and proportions of aquatic prey were compared for the AOC & SA in EMC and two such models were compared for the OOC REF. The absolute differences between the two sets of models' predictions were 2.6 (1.6) and 3.3 (0.6) pg/g PCB TEQ in EMC and the OOC REF, respectively. For the EMC, the diet and bioaccumulation models' predictions (the latter was optimized to match EMC diet model results) differed by 4.3 (3.3) % of the diet model

results. Predictions of the EMC model applied to the OOC REF differed by 94 (1.0) % because while the absolute differences were of the same magnitude as for EMC, the diet model results in OOC REF were two orders of magnitude smaller than in EMC (Table 10).

BUI removal criteria hypotheses relevant to this study

Hypothesis 10: *PCB concentrations in fish tissue and other prey are below thresholds likely to result in **acute** toxicity to fish or piscivorous wildlife (birds and **mammals**).* UF in the EMC AOC have a higher concentration of TPCB than the 5,000 ng/g acute LOAEC for Arochlor 1254 which is the most toxic Arochlor (Tables 5 and 6).

Hypothesis 11A: *PCB concentrations in fish tissue from comparable functional feeding groups are similar to reference sites*. TPCB and PCB TEQ concentrations in CR, LF and UF are significantly higher in the EMC AOC than in the OOC REF, GR portion of the RE AOC and BR AOC (Table 6).

Hypothesis 11B: *PCB concentrations in fish or other prey are below tissue concentrations known to cause deformities or reproductive impairment in piscivorous wildlife (birds and **mammals**).* The chronic LOAECs for TPCB and PCB TEQ known to cause deformities or reproductive impairment in mink are 960 ng/g and 9.2 pg/g, respectively. In the EMC AOC, concentrations of TPCB in LF and UF are 1.8 and 6.6 times greater, respectively, than the chronic LOAEC and concentrations of PCB TEQ in LF and UF are 1.2 and 55.4 times greater, respectively, than the chronic LOAEC (averages of values in Tables 5 and 6).

Can BUIs for the EMC AOC be removed?

In relation to their current removal criteria (Table 1), the combined field results from this study and E & E (2019) support removal of BUI #3 and do not support removal of BUI #5 in the EMC AOC. The concentration of TPCB in UF fish in the AOC exceeds the acute LOAEC used in this report (5,000 ng/g for Arochlor 1254; Aulerich and Ringer 1977) by ~24% (Table 6) while the concentration of TPCB in LF is ~35% of the acute LOAEC. Mink eating a diet high in LF and UF in the AOC are potentially at risk of consuming a lethal diet, a prospect also explored by the diet and bioaccumulation models. Considering all prey groups, the diet model for the AOC predicted that mink consuming a 57% typical aquatic diet would consume ~50% of the acute TPCB LOAEC concentration, while a mink consuming a 92% worst case aquatic diet would consume ~92% of the acute LOAEC (Table 9).

A comprehensive weight-of-evidence approach should be used by the EMC RAP Coordinating Committee to determine whether the BUIs addressed in this study can be removed using data presented in this report. First, the last two digits in an Arochlor number (except for 1016) indicate the mixture's percent chlorination which correlates well with its toxicity and means that different Arochlors have different LOAECs; e.g., 10,000 ng/g and 20,000 ng/g for Arochlors 1242 and 1016, respectively (Bleavins *et al*. 1980). Second, the typical Arochlor measured in AOC sediments has been 1248 (personal communication, Scott Pickard, USACE, Buffalo District). Thus, the mixture of Arochlors in AOC prey consumed by mink is likely

to be considerably less acutely toxic to them than 1254 alone. It is recommended that the following factors be considered when evaluating the removal of BUIs #3 and #5:

1. BUI #3—Based on the current wording of Criterion 3 of this BUI, *"PCB concentrations in fish tissue and other prey are below thresholds likely to result in **acute** toxicity to fish or piscivorous wildlife (birds and **mammals**)"*, it is unclear whether "PCB" refers to total, TEQ or both. TPCB exceeded the acute 5,000 ng/g LOAEC for Arochlor 1254 in AOC UF samples (Table 6), but not in the aquatic diet models (Tables 8 and 9). Given that other less toxic Arochlors, particularly 1248, predominate in the AOC, it is highly unlikely that a mink living in the AOC would suffer acute effects from TPCB. In support of this point, for several reasons presented earlier in this report, PCB TEQ is a much better measure of toxicity to wildlife than TPCB (Giesy and Kannan 2002). For PCB TEQ, concentrations in our mink prey samples and diet model predictions in the AOC were always below the acute LOAEC of 1,000 pg/g for PCB TEQ.

   In addition, and as discussed previously, AOC UF fish was the only prey group to exceed the acute LOAEC for TPCB (5,000 ng/g, Arochlor 1254). Projections including data from all prey groups employed in our models predict that the TPCB would fall below this LOAEC.

   Based on this information, a mink consuming aquatic prey in the EMC AOC would be highly unlikely to suffer acute toxicity from TPCB or PCB TEQ, and Criterion 3 for BUI #3 is recommended for removal in the EMC AOC.

2. BUI #5—Criterion 1 of this BUI, *"PCB concentrations in fish tissue from comparable functional feeding groups are similar to reference site(s)"*, is not recommended for removal based on the results of this study. PCB (total and TEQ) concentrations in the AOC are significantly higher than in two other AOCs (BR AOC; GR portion of the RE AOC) and the OOC REF.

3. BUI #5—Criterion 2 of this BUI, *"PCB concentrations in fish and other prey are below tissue concentrations known to cause deformities or reproductive impairment* [chronic effects] *in piscivorous wildlife."* The currently established chronic TPCB and PCB TEQ LOAECs for deformities and reproductive impairment in piscivorous wildlife, of which mink are the most sensitive species in North America, are 960 ng/g and 9.2 pg/g TEQ, respectively (Bursian *et al.* 2006). In the AOC, TPCB concentrations in LF and UF exceeded the chronic LOAEC by factors of 1.2 and 6.6, respectively. Similarly, PCB TEQ exceeded its chronic LOAEC by factors of 1.2 and 55.4, respectively. Diet model predictions for the AOC and SA (averages of the five values in Tables 8 and 9) exceeded the chronic TPCB and PCB TEQ LOAECs by factors of 3.4 and 6.5, respectively. Accordingly, a mink living in the AOC would be likely to suffer deformities and reproductive impairment and this BUI is not recommended for removal.

Other than waiting decades or centuries for natural ecosystem processes to bury or degrade PCBs in upstream source areas, the lowering of water PCB concentrations and, thus, fish

tissue PCB concentrations to levels in the AOC that would allow removal of either BUI #5 Criterion 1 OR Criterion 2 would require accurate identification and remediation of those source areas, an expensive prospect. Upstream areas are currently being evaluated by the USEPA through the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA/ Superfund) process. Remedial design for the Creek Corridor (stream reach OU2) and remedial investigation from the city of Lockport to Lake Ontario (stream reach OU3) are underway, including a Human Health Risk Assessment (HHRA) and Baseline Ecological Risk Assessment (BERA), and proposed remedial alternatives for the creek and its floodplain are nearing completion (Eighteen Mile Creek Superfund Site, www.epa.gov/superfund/eighteenmile-creek and click "Site Documents & Data").

Recommendations and Conclusions

1. Based on the results this study, BUI #3, Criterion 3, *"PCB concentrations in fish tissue [UF in the EMC AOC] are below thresholds likely to result in **acute** toxicity to fish or piscivorous wildlife (birds and **mammals**)"* is true and is recommended for removal in the EMC AOC. Although the concentration of TPCB in the UF prey group in the AOC exceeds the acute LOAEC when considered in isolation, weight-of-evidence indicates that PCBs in the AOC are not likely to cause acutely toxicity in mink.
2. Based on the results of this study, BUI #5, Criteria 1 "*PCB concentrations in fish tissue from comparable functional feeding groups are similar to reference sites*" OR 2 "*PCB concentrations in fish or other prey are below tissue concentrations known to cause deformities or reproductive impairment in piscivorous wildlife*" are not recommended for removal. Concentrations of TPCB and PCB TEQ are significantly higher in the EMC AOC than the GR portion of the RE AOC, BR AOC and OOC REF (Criterion 1), and concentrations of TPCB and PCB TEQ in the AOC substantially exceed their chronic LOAECs (Criterion 2).
3. A better alternative to looking at tissue concentrations in separate trophic groups to "guestimate" whether mink may be adversely affected chronically (health) or acutely (lethal) in the AOC would be to consider the results of the diet and bioaccumulation models used in this study that reflect literature-based typical- and worst-case aquatic diets and bioconcentration of PCB TEQ from water based on co-planar PCB k_{ow}s for mink living in riverine-lacustrine habitats like the AOC. By considering all trophic levels in the mink diet, concentrations of TPCB predicted for their tissue are near (92% aquatic diet) or about half (57% aquatic diet) of the most conservative (in terms of protecting mink health) 5,000 ng/g acute LOAEC for Arochlor 1254 (Aulerich and Ringer 1977). For PCB TEQ, modeled concentrations ranged by factors of 4.0 to 9.2 higher than the 9.2 pg/g chronic LOAEC. Given that exposure to TEQ PCB by aquatic biota is a better way to determine risk to mink than exposure to TPCB (Giesy and Kannon 2002), perhaps the

independently modeled PCB TEQ data in Tables 8 and 9 are what the RAP Coordinating Committee should weigh most highly while considering whether to remove BUI #5.

Relevant to BUI #5 Removal Criterion 2, getting PCB TEQ, not TPCB, below chronic LOAECs in contaminated ecosystems is now considered the best way to protect the health of piscivorous birds and mammals. In the future, the RAP Coordinating Committee should consider using water sampling and our bioaccumulation model that was optimized for the EMC AOC to predict PCB TEQ in mink. Given currently high TEQ in mink prey it will take many years for predicted PCB TEQ to fall below the LOAEC, at which time another mink prey study should be conducted so that then existing PCB TEQ concentrations in mink prey can be used in our diet model. If the bioaccumulation and diet models at that time agree that PCB TEQ concentrations are less than the chronic LOAEC, BUI #5 Removal Criterion 2 would be satisfied.

An alternative to the approach described above would be to locate and remediate source areas in EMC to reduce PCB concentrations in water and, subsequently, mink prey in the AOC below the chronic LOAECs for mink, which would be a long and costly process.

4. Another approach for the RAP Coordinating Committee to consider would be to examine the findings reported in the mink habitat suitability and signs portion of this study (Haynes and Wellman 2019) that led the project team to decide that a mink prey study was the only way to address BUIs #3 and #5. Mink habitat suitability was low, only one definitive mink sign (tracks in mud, ~100 m below Burt Dam) was observed, and the area of the AOC is so small that only 1-2 male mink at a time could hold territories there. While some mink may pass through the AOC to reach other habitats, the AOC itself cannot sustain a viable mink population and the same is true for this study's "source area" between Ide Road and Burt Dam (Figure 1). While any mink living long-term in the AOC would exceed the chronic LOAEC for PCB TEQ, the RAP Coordinating Committee should consider removing BUI #5, Criterion 2 on the basis that few or no mink can be long-term residents of the AOC due to habitat quality and area constraints.

Acknowledgments

We thank Brockport graduate research assistants Paige Buchholz and Madelynn Edwards for collecting mink prey and water samples and processing them in the lab before shipment to ALS Environmental for analysis. We are grateful for Randall Baase's willingness to share his expertise on mink habitat, habits and signs, indebted to Jeffrey Wellman for creating the bioaccumulation model macro and saving weeks of iteration time, obliged to Scott Pickard (USACE) and David Clarke (NYDEC) for detailed, constructive critical reviews of earlier drafts, and thankful for devoted attention to this project by Scott Collins, the EMC AOC RAP Coordinator.

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Tables

Table 1. EMC AOC removal criteria for BUIs 3 and 5 as of 03/21/21.

BUI 3. Degradation of Fish and Wildlife Populations

Status: Impaired

Removal Criteria: Fish community metrics (e.g., diversity, abundance, biomass, and condition) are similar to reference site(s); **AND**

Benthic macroinvertebrate community composition is within the range expected and similar to reference site condition; **AND**

PCB concentrations in fish tissue and other prey are below thresholds likely to result in acute toxicity to fish or piscivorous wildlife (birds and mammals).

BUI 5. Bird or Animal Deformities or Reproductive Problems

Status: Impaired

Removal Criteria: PCB concentrations in fish tissue from comparable functional feeding groups are similar to reference site(s); **OR**

PCB concentrations in fish and other prey are below tissue concentrations known to cause deformities or reproductive impairment in piscivorous wildlife.

Table 2. Definitions of acronyms used in this report.

AhR: Aryl hydrocarbon Receptor
AM: Amphibian
Acute LOAEC: Lowest Observed Adverse Effect (dietary) Concentration that kills an organism
AOC: Area of Concern
BAF: Bioaccumulation Factor (diet to tissue)
BCF: Bioconcentration Factor (water to tissue)
BERA: Baseline Ecological Risk Assessment
BR AOC: Buffalo River AOC
BUI: Beneficial Use Impairment
CDD: Chlorinated Dibenzo Dioxins
CDF: Chlorinated Dibenzo Furans
CERCLA: Comprehensive Environmental Response, Compensation and Liability Act ("Superfund")
Chronic LOAEC: Lowest Observed Adverse Effect (dietary) Concentration that harms an organism
COC: Chemical of Concern
CR: Crayfish
DAPC: Dunn's All-Pairwise Comparison
EMC: Eighteenmile Creek (Area of Concern = AOC and Source Area = SA)
FCM: Food Chain Multiplier
GR AOC: Genesee River portion of the Rochester Embayment AOC
HHRA: Human Health Risk Assessment
IJC: International Joint Commission
KW: Kruskal-Wallis AOV (Analysis of Variance of Ranks)
LF: Lower Trophic Level Fish
LMB: Largemouth Bass
Log K_{ow}: Logarithm of the octanol-water partition coefficient of a chemical
OOC REF: Oak Orchard Creek Reference Area
NP: Northern Pike
PCB: Polychlorinated Biphenyls
RAP: Remedial Action Plan
TEF: Toxic Equivalency Factor
TEQ: Toxic Equivalents
THg: Total Mercury
TL: Trophic Level
UF: Upper Trophic Level Fish
USACE: U.S. Army Corps of Engineers
USEPA: U.S. Environmental Protection Agency
WRS: Wilcoxon Rank Sum Test

Table 3. Dates and locations of water and biological sampling.

	Spring	Summer	Fall
Water (1 gal. each)			
EMC			
Source Area	2019: 5/16	2019: 7/29	2018: 10/10
AOC	2019: 5/15	2019: 7/31	2018: 10/10
Lake Ontario	2019: 5/15 (off Eighteenmile Creek)	2019: 8/5 (off Braddock Bay)	2020: 10/13 (off Sandy Creek)
OOC (USACE)	2021: 3/16	2020: 8/10	
Mink Prey			
Amphibians[a]			
Source Area	2019: 5/23-24 (10)	2019: 7/29 (0)	2018: 9/22 (0)
	2020: 3/26-4/8 (10)		2019: 9/25 (4 juv.)
AOC	2020: 5/20 (1)	2019: 7/31 (0)	2018: 9/22 (0)
Crayfish[b]			
Source Area	2019:5/23 (~40)	2019: 7/29 (~30)	2018: 9/22 (42)
AOC	2020: 5/20 (32)	2019: 7/31 (39)	2018: 9/21 (33)
Fish[c]			
Source Area	2019: 5/16 (15)	2019: 7/29 (15)	2019: 9/25 (15)
AOC	2019: 5/15 (15)	2019: 7/31 (15)	2018: 10/6 (15)
Oak Orchard Creek			
Crayfish[b]	2020: 6/4 (40)	2020: 7/30 (50)	2020: 10/2 (40)

[a]In the Source Area, adult frogs and toads were seen only in the spring; no frogs were seen in the summer and only four, very small young-of-the-year frogs were seen in the fall. In the AOC, only two toads were seen across the three seasons sampled. Species of frogs collected were leopard frog (*Lithobates pipiens*), green frog (*L. clamitans*) and American toad (*Anaxyrus americanus*)

[b]The species of crayfish collected was the Northern clearwater crayfish, *Orconectes propinquus*.

[c]Species of lower trophic level fish collected across three seasons (N=60) were mostly bluegill (*Lepomis macrochirus*) and pumpkinseed (*L. gibbosus*), plus six yellow perch (*Perca flavescens*) and one rock bass (*Ambloplites rupestris*). Species of upper trophic level fish collected across three seasons (N=30) were mostly largemouth bass (*Micropterus salmoides*) and smallmouth bass (*M. dolomieu*), plus four northern pike (*Exox lucius*).

Table 4. Fishes caught for chemical analysis in Eighteenmile Creek during the mink prey study.

		Season		
Location	**Spring**	**Summer**	**Fall**	**Percent**
Upper Trophic Level				
Area of Concern				
Northern Pike	1		1	13.3%
Largemouth Bass	2	3	4	60.0%
Smallmouth Bass	2	2		26.7%
Source Area				
Northern Pike	1			6.7%
Largemouth Bass	4	2	5	73.3%
Smallmouth Bass		3		20.0%
Lower Trophic Level				
Area of Concern				
Bluegill	4	4	3	36.7%
Pumpkinseed	6	4	4	46.7%
Yellow Perch		1	3	13.3%
Rock Bass		1		3.3%
Source Area				
Bluegill	10	5	6	70.0%
Pumpkinseed		3	3	20.0%
Yellow Perch		2	1	10.0%

Table 5. Mean (SD) trophic level and concentrations of chemicals of concern of mink prey collected in this study.

Numbers in red exceed chronic LOAECs: 500 ng/g THg; 960 ng/g TPCB; 9.2 pg/g of PCB, CDD or CDF TEQ, combined or separately. Numbers in **red bold** exceed acute LOAECs: 5,000 ng/g TPCB. NSC = No Samples Collected.

Category	Crayfish Mean (SD)	P	Result	Lower TL Fish Mean (SD)	P	Result	Upper TL Fish Mean (SD)	P	Result	Amphibians Mean (SD)
Trophic Level										
EMC AOC	3.98 (0.06)			4.82 (0.81)			5.14 (0.27)			ND
EMC SA	3.80 (0.21)		OOC>SA;	4.43 (0.11)		AOC>SA	5.20 (0.06)			2.5 (0.1)
OOC REF	4.37 (0.06)	0.0067	AOC=SA&OOC	NSC	0.854	suggested	NSC	0.7	AOC=SA	NSC
Total Mercury (ng/g)										
EMC AOC	35.8 (38.3)			50.1 (31.2)			215.3 (71.9)			NSC
EMC SA	30.2 (26.0)			64.3 (12.6)			234.3 (58.1)			129.5 (105.4)
OOC REF	13.5 (2.7)	0.6262	AOC=SA=OOC	NSC	1	AOC=SA	NSC	1	AOC=SA	NSC
Total PCB (ng/g)										
EMC AOC	293 (170)			619 (534)			**6,395** (4,977)			NSC
EMC SA	1,210 (1,413)		SA>OOC;	2,307 (950)			3,830 (468)			107.2 (77.5)
OOC REF	7.7 (3.7)	0.0067	AOC=SA&OOC	NSC	0.2	AOC=SA	NSC	0.7	AOC=SA	NSC
PCB TEQ (pg/g)										
EMC AOC	5.2 (6.7)			12.2 (15.7)			136.7 (158.7)			ND
EMC SA	10.4 (8.6)		SA>OOC;	57.0 (44.4)			164.7 (118.5)			7.2 (7.1)
OOC REF	0.3 (0.02)	0.0155	AOC=SA&OOC	NSC	0.2	AOC=SA	NSC	1	AOC=SA	NSC
CDD/CDF TEQ (pg/g)										
EMC AOC	0.7 (0.2)			0.7 (0.5)			3.4 (2.1)			NSC
EMC SA	0.6 (0.5)			1.8 (1.0)			2.3 (1.8)			0.9 (0.8)
OOC REF	0.07 (0.02)	0.7	AOC=SA=OOC	NSC	0.1	AOC=SA	NSC	0.7	AOC=SA	NSC
Total TEQ (pg/g)										
EMC AOC	5.9 (6.8)			12.9 (16.0)			140.2 (159.0)			NSC
EMC SA	11.0 (8.3)		SA>OOC	58.9 (43.5))	0.2	AOC=SA	167.0 (118.9)	1	AOC=SA	8.1 (7.0)
OOC REF	0.4 (0.06)	0.0155	AOC=SA&OOC	NSC			NSC			NSC

Table 6. Mean (SD) concentrations of chemicals of concern collected by Brockport (2013-2014) and E & E (2019).
Numbers in red exceed chronic LOAECs: 500 ng/g THg; 960 ng/g TPCB; 9.2 pg/g total PCB/CDD/CDF TEQ combined or separately. Numbers in **red bold** exceed acute LOAECs: 5,000 ng/g TPCB. NSC = No Samples Collected.

Category	Lower TL Fish Mean (SD)	P	Result	Upper TL Fish Mean (SD)	P	Result
Total Mercury (ng/g)						
EMC AOC	25.8 (20.1)			279 (130)		
EMC SA	26.5 (22.4)			310 (117)		
OOC REF	20.5(2.1)			384 (106)		
GR AOC	272 (26)		GRAOC>BRAOC=EMCSA=	567 (44)		EMCAOC=EMCSA> BRAOC=
BR AOC	84.4 (8.9)	0.0007	EMCAOC=OOCREF	265 (112)	0.1718	GRAOC= OOC REF
Total PCB (ng/g)						
EMC AOC	1,752 (623)			**6,219** (3,382)		
EMC SA	2,902 (1,084)			**6,911** (4,184)		
OOC REF	714 (78)			502 (157)		
GR AOC	88 (16)		EMCSA=EMCAOC>	332 (33)		EMCAOC=EMCSA>BRAOC=GRAOC=
BR AOC	381 (248)	<0.0001	BRAOC=GRAOC=OOCREF	993 (184)	0.0001	OOC REF
PCB TEQ (pg/g)						
EMC AOC	12.0 (10.0)			373 (312)		
EMC SA	48.8 (28.2)			446 (355)		
OOC REF	0.8 (n=1)			8.6 (0.5) (n=2)		EMCSA=EMCAOC>GRAOC
GR AOC	3.3 (5.4)		EMCSA=EMCAOC>			EMCSA=EMCAOC=OOCREF=BRAOC
BR AOC	0.4 (0.2)	0.0002	GRAOC=OOCREF=BRAOC	6.1 (3.3)	0.0002	OOCREF=BRAOC=GRAOC

Table 6 continues on next page

Category	Crayfish Mean (SD)	P	Result	Amphibians Mean (SD)	P	Result
Total Mercury (ng/g)						
EMC AOC	35.8 (38.2)			NSC		
EMC SA	30.2 (26.0)			130 (105)		
OOC REF	13.5 (2.7)			NSC		
GR AOC	114.7 (16.9)		GRAOC>EMCAOC=	74 (11)		
BR AOC	NSC	0.0398	EMCSA>OOCREF	NSC	1.0	EMCSA=GRAOC
Total PCB (ng/g)						
EMC AOC	489 (293)			NSC		
EMC SA	835 (975)			107 (28)		
OOC REF	7.9 (3.8)		EMCSA=EMCAOC >	NSC		
GR AOC	23.9 (4.5)	<0.0001	GRAOC=OOCREF	4.8 (1.2)	0.2	EMCSA=GRAOC
BR AOC	NSC			NSC		
PCB TEQ (pg/g)						
EMC AOC	5.2 (6.7)			NSC		
EMC SA	10.4 (8.6)			7.2 (7.1)		
OOC REF	0.3 (0.02)		EMCSA=EMCAOC >	NSC		
GR AOC	0.2 (0.2)	0.0038	GRAOC=OOCREF	0.2 (0.3)	0.2	EMCSA=GRAOC
BR AOC	NSC			NSC		

Table 7. Mean (SD) chemical of concern concentrations in whole water collected during this study and by USACE[a] and USEPA[b].

Brockport Data	**Mean (SD)**	**P**	**Result**
THg (pg/mL)			
EMC AOC	1.1 (1.2)		
EMC SA	1.8 (1.1)		
L. Ontario	1.3 (0.7)	0.5824	EMCAOC=EMCSA=LO
Total PCB (pg/mL)			
EMC AOC	35.4 (7.2)		
EMC SA	66.8 (6.6)		
LO	0.3 (0.2)	0.0010	AOC = SA > LO
PCB TEQ (fg/mL)			
EMC AOC	0.16 (0.03)		
EMC SA	0.17 (0.15)		
L. Ontario	0.07 (0.07)	0.1016	EMCAOC=EMCSA=LO
CDD/CDF TEQ (fg/mL)			
EMC AOC	0.54 (0.31)		
EMC SA	0.37 (0.25)		
L. Ontario	0.48 (0.41)	0.7615	EMCAOC=EMCSA=LO
USEPA, USACE & Brockport Data			
TPCB (pg/mL)			
EMC AOC	47.4 (10.3)		
OOC REF	0.29 (0.1)		
L. Ontario	0.3 (0.2)	<0.0001	EMC AOC > OOC REF = LO

[a]Data for fall 2020 and spring 2021 were provided by Andrew Lenox, USACE, Buffalo, NY District.

[b]Data for 2005-2010 were in USEPA. 2011. Final Data Report, Lake Ontario Tributaries, 2009-2010 (Report provided by Andrew Lenox, USACE, Buffalo District).

Table 8. Diet model estimates of mink exposures in EMC. Values in red for TPCB (Arochlor 1254) and PCB TEQ exceed their chronic LOAECs. No TPCB and PCB TEQ values exceed the acute LOAEC. All diets were derived from composited samples of crayfish, lower trophic level fish (bluegill and pumpkinseed) and upper trophic level fish (largemouth bass and northern pike) collected for this study.

	Trophic Level	THg (ng/g)	Total PCB (ng/g)	TEQ from PCB (pg/g)	TEQ from CDD/CDF (pg/g)
LOAECs					
Chronic		500	960	9.2	9.2
Acute		1,000	5,000	1,000	1,000
DIET					
SA with Amphibians					
65% Aquatic	3.6	100.3	1,719	64.2	1.1
TL = 4	4.0	121.4	2,226	85.6	1.4
92% Aquatic	4.6	157.5	2,888	111.0	1.9
SA No Amphibians					
57% Aquatic	3.6	89.8	1,710	63.6	1.1
TL = 4	4.0	119.1	2,237	85.9	1.4
92% Aquatic	4.7	158.8	2,982	114.5	1.9
AOC No Amphibians					
57% Aquatic	3.6	82.1	2,243	47.7	1.3
TL = 4	4.0	104.4	2,897	61.7	1.6
92% Aquatic	4.8	143.7	3,989	84.9	2.3

Table 9. Diet model comparison of EMC with OOC.
Values in red exceed the chronic LOAEC for TPCB (Arochlor 1254) and PCB TEQ. The **red bold** value exceeds the acute LOAEC for Arochlor 1254. Diets are based on composited samples of crayfish and pumpkinseed collected for this study and by E & E (2019), respectively. Largemouth bass fillet data from E & E (2019) were converted to composited whole-fish data before multiplying by a correction factor of 2.8 (Skinner *et al*. 2009).

	THg (ng/g)	**Total PCB** (ng/g)	**TEQ from PCB** (pg/g)
LOAECs			
Chronic	500	960	9.2
Acute	1000	5,000	1000
DIET			
EMC SA			
57% Aquatic	117	3,126	80.0
92% Aquatic	196	**5,563**	142.9
EMC AOC			
57% Aquatic	124	2,561	37.0
92% Aquatic	217	4,619	65.9
OOC			
57% Aquatic	140	11	0.1
92% Aquatic	250	22	0.2

Table 10. Comparison of diet model and bioaccumulation model estimates of mink dietary exposure to PCB TEQ[a] (pg/g).

		EMC SA		EMC AOC		OOC REF[a]	
Amphibians Included	Yes	No	No	No	No	No	No
Trophic Level	3.6	3.6	4.0	3.6	4.0	3.6	4.0
% Aquatic Prey	65	57	69	57	67	57	65
Diet Model PCB TEQ (pg/g)	64.2	63.6	85.9	47.7	61.7	3.0	3.8
Bioaccumulation Model PCB TEQ (pg/g)	66.6	59.6	87.9	43.5	62.0	0.2	0.2
Absolute Difference (pg/g)[b]	2.4	4.0	2.0	4.2	0.3	2.8	3.6
% Difference[c]	3.7	6.2	2.3	8.8	0.5	93.3	94.7

[a]OOC REF bioaccumulation was calculated using the model optimized for EMC SA and AOC based on samples we collected in EMC. The OOC REF diet model used data from crayfish collected in our study along with composited pumpkinseed and largemouth bass fillet samples (converted to whole fish concentrations per Skinner *et al.* 1996) collected by E & E (2019).

[b]Absolute difference between diet and bioaccumulation models: EMC mean (SD) = 2.6 (1.6) pg/g; OOC REF mean (SD) = 3.2 (0.6) pg/g

[c]Difference between models as percent of the diet model result: EMC mean (SD) = 4.3 (3.3) %; OOC REF mean (SD) = 94.0 (1.0) %.

Figures

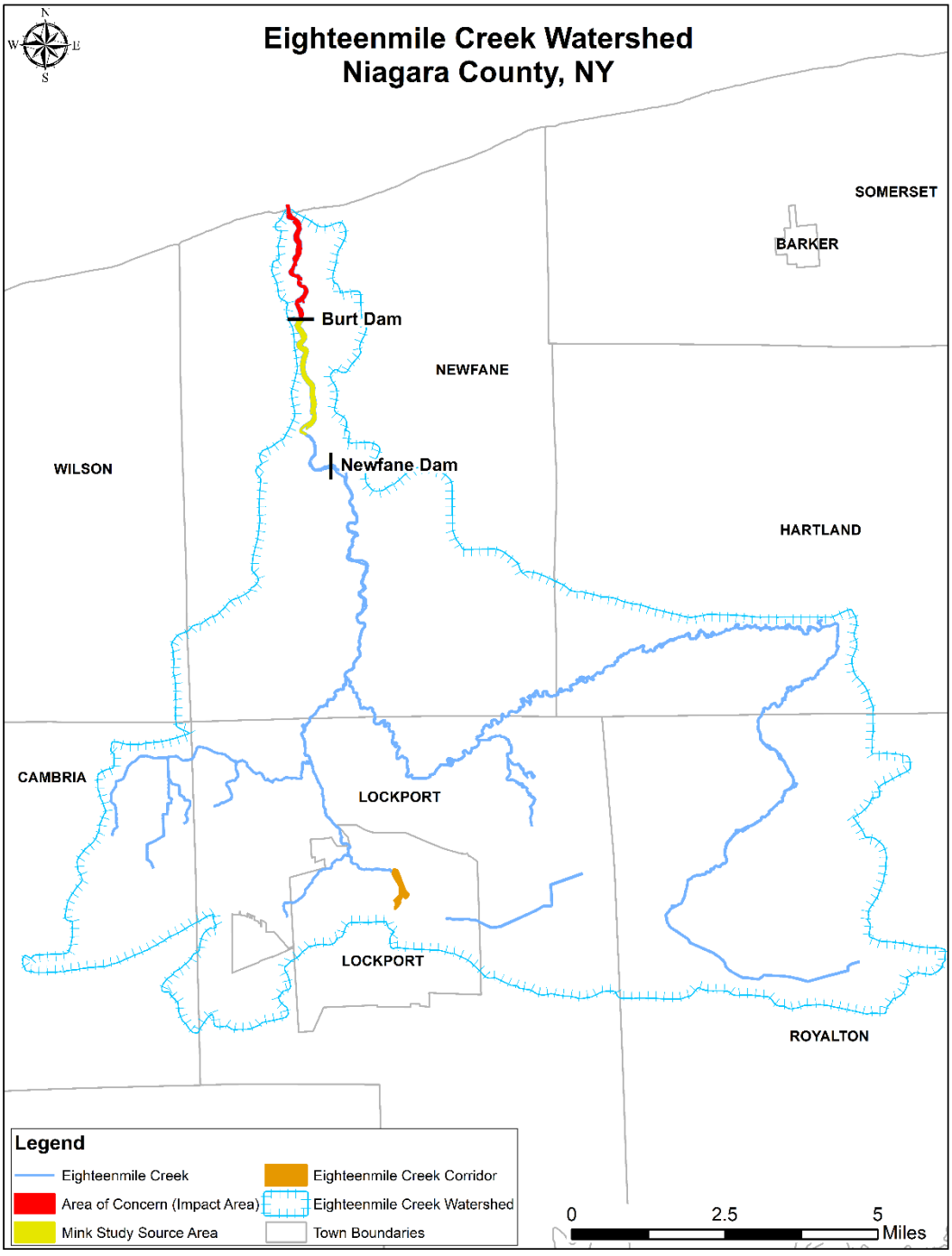


Figure 1. Map of the Eighteenmile Creek watershed.
For this project, the portion of the Source Area sampled was from Burt Dam to ~1 mi. below Newfane Dam. Map created by Scott Collins, Niagara County Soil and Water Conservation District, Lockport, NY.

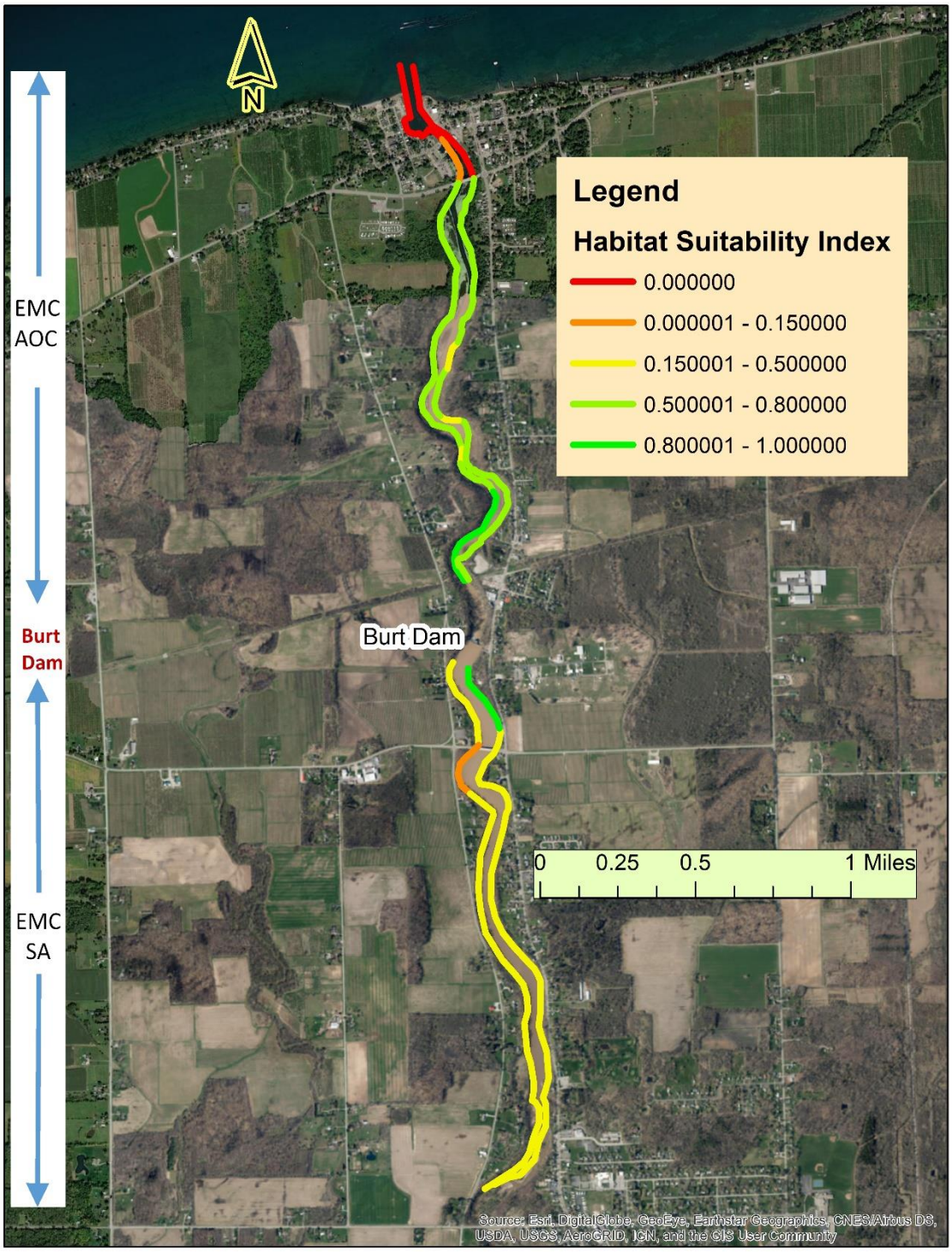


Figure 2. Mink habitat suitability index (HSI) scores.

The AOC extends north of Burt Dam to Lake Ontario and the Source Area extends south of Burt Dam to Ide Road which runs east-west along the bottom of the map. Colored lines indicate HSI scores.

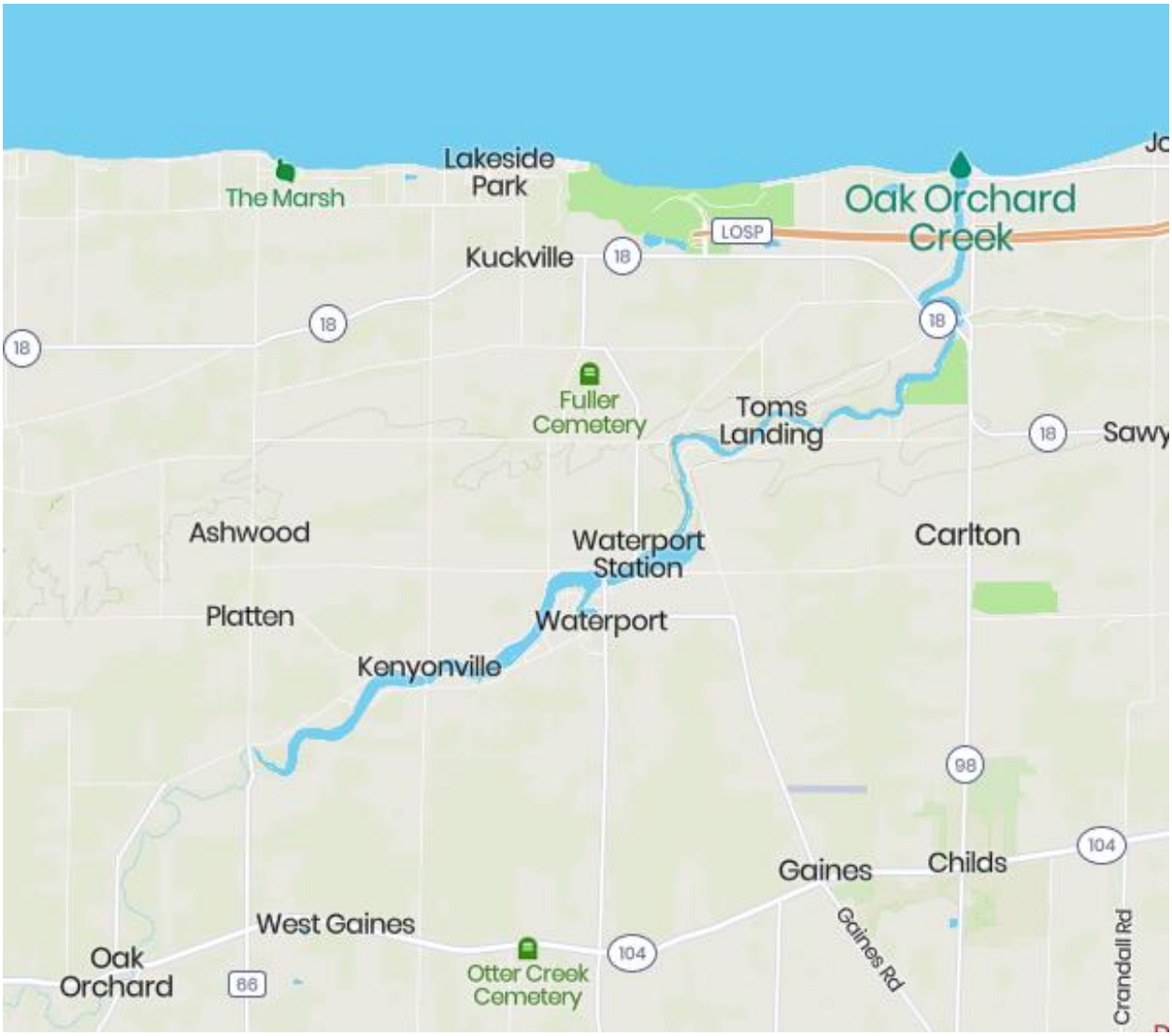


Figure 3. Map of the Oak Orchard Creek watershed.

For this project, Brockport sampled crayfish in the portion of Oak Orchard Creek that extended ~1 mi. below the Waterport Station Dam.

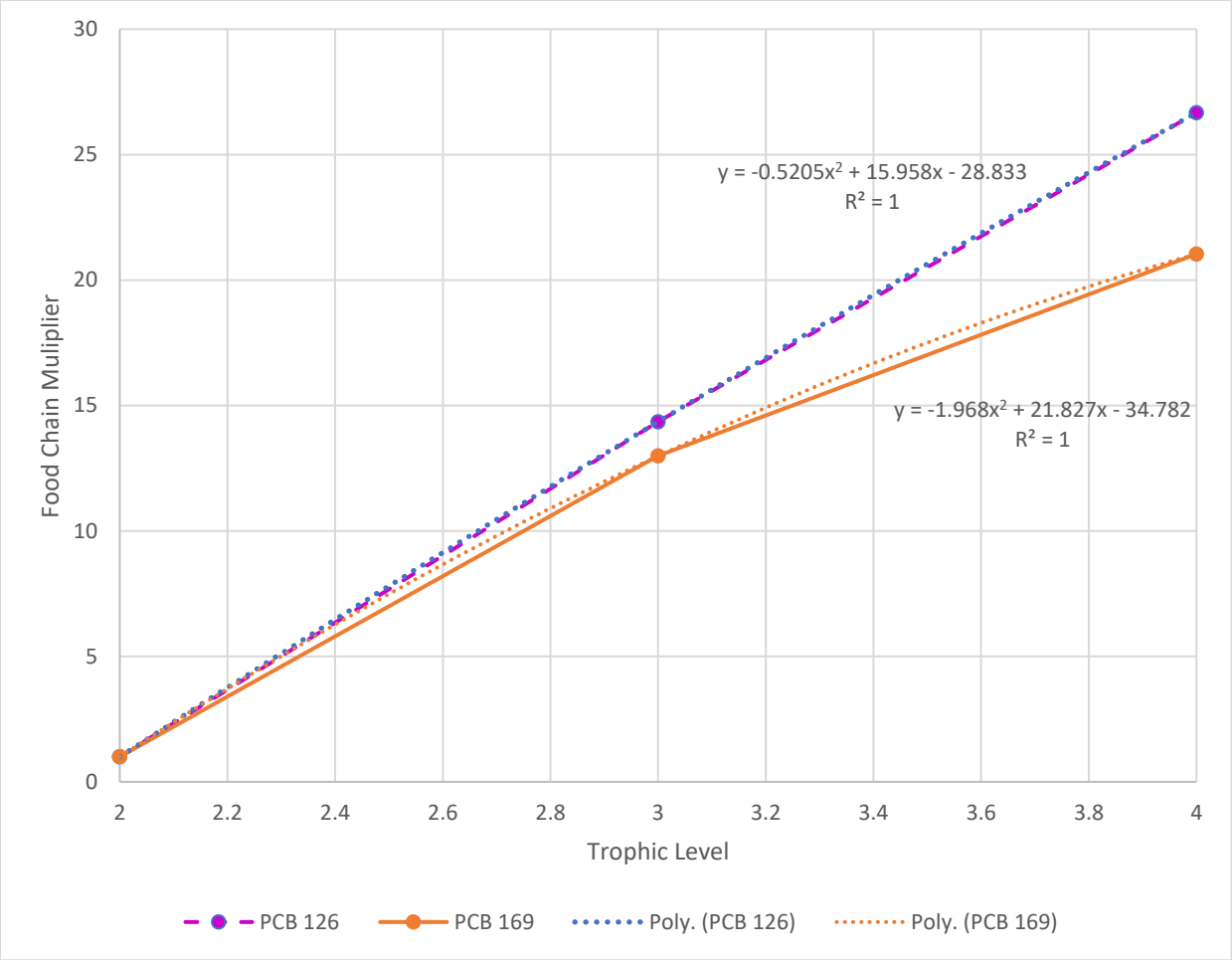


Figure 4: Non-linearity of Food Chain Multipliers vs. Trophic Level.
FCMs had to be interpolated for diets with trophic level of 3.6. This was done indirectly inside the bioaccumulation model.

Figure 5. Correlation (R = 0.73) of bioaccumulation model and diet model predictions for PCB congener concentrations.

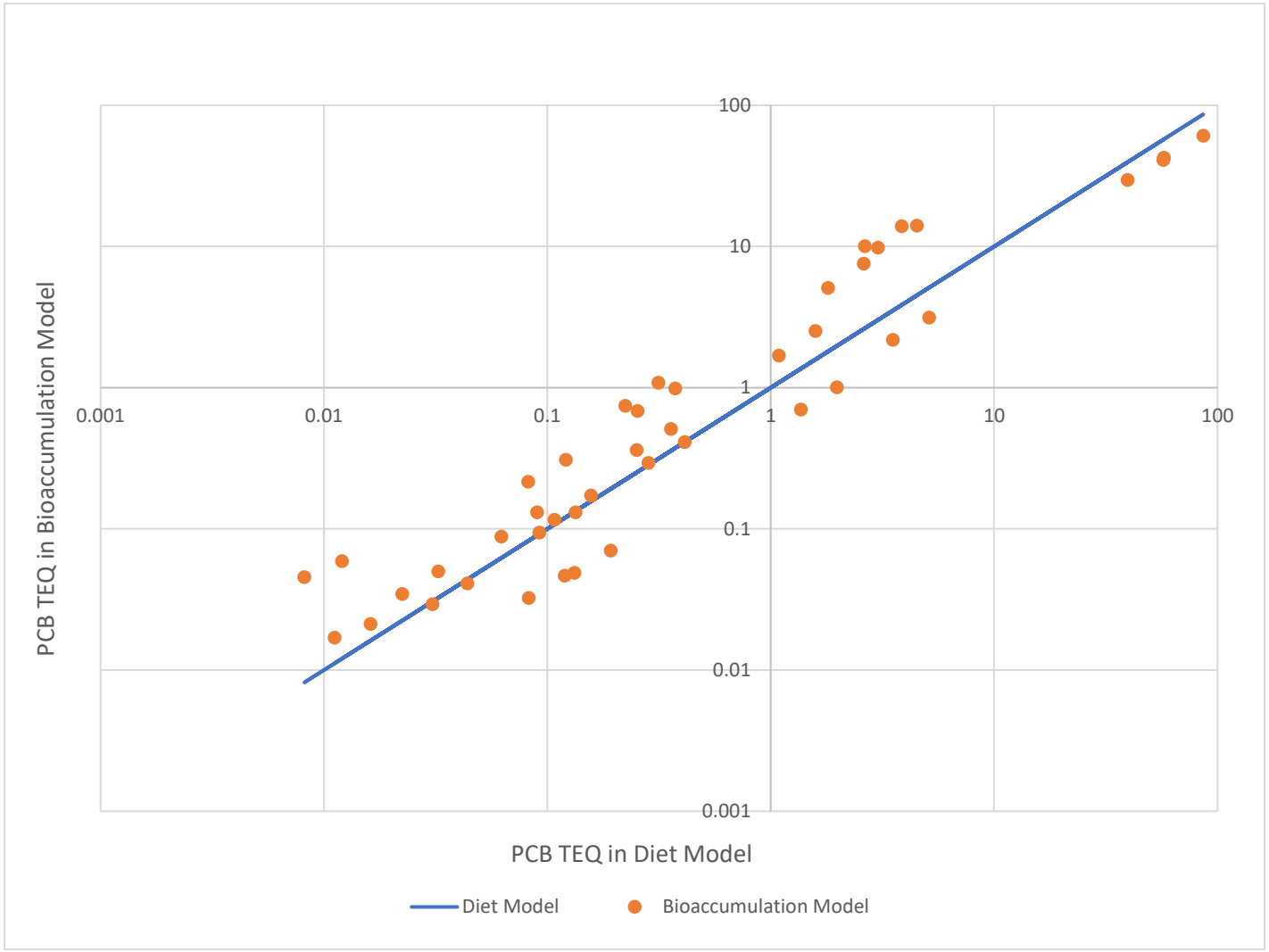


Figure 6. Correlation (R = 0.98) of bioaccumulation model and diet model predictions for PCB congener TEQ.

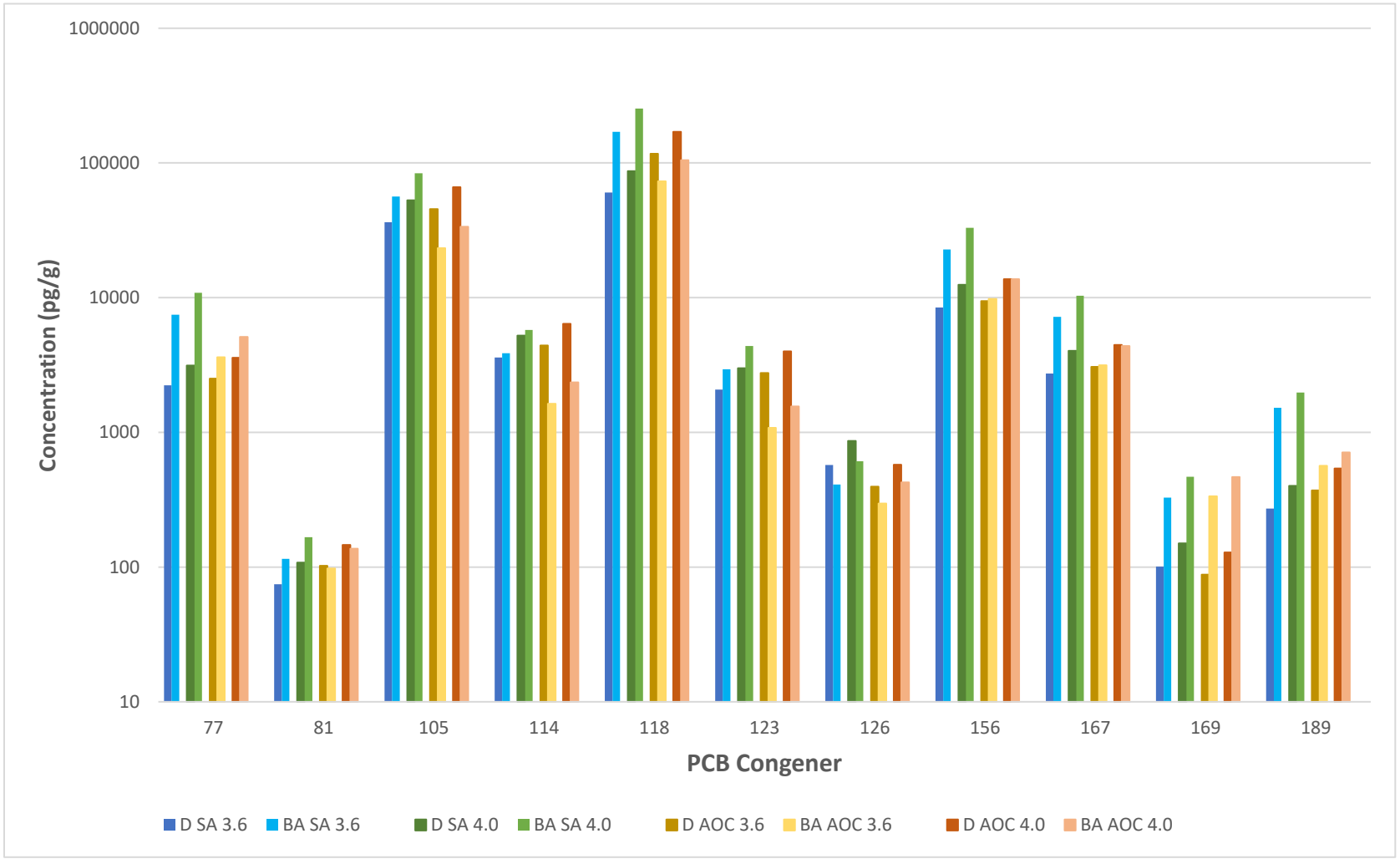
Appendices

Appendix A: Chemical Data and Modeling Calculations (electronic).

Appendix B: Statistical Calculations (electronic).

Appendix C: PCB Congener and PCB TEQ Modeling Results (next 2 pages).

Appendix C1. Concentrations of PCB congeners predicted by diet and bioaccumulation models.
Legend: D = Diet model, BA = Bioaccumulation model, SA = source area, AOC = area of concern, 3.6 and 4.0 are trophic levels.



Appendix C2. TEQ from PCB congeners predicted by diet and bioaccumulation models.

Legend: D = Diet model, BA = Bioaccumulation model, SA = source area, AOC = area of concern, 3.6 and 4.0 are trophic levels.