

Hazard/Risk Assessment

CHEMICAL AMPLIFICATION IN AN INVADDED FOOD WEB: SEASONALITY AND ONTOGENY IN A HIGH-BIOMASS, LOW-DIVERSITY ECOSYSTEM

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Abstract—The global spread of invasive species is changing the structure of aquatic food webs worldwide. The North American Great Lakes have proved particularly vulnerable to this threat. In nearshore areas, invasive benthic species such as dreissenid mussels and round gobies (*Neogobius melanostomus*) have gained dominance in recent years. Such species are driving the flow of energy and material from the water column to the benthic zone, with dramatic effect on nutrient and contaminant cycling. Here, we develop a stage-structured model of a benthified food web in Lake Michigan with seasonal resolution and show how its bioaccumulation patterns differ from expected ones. Our model suggests that contaminant recycling through the consumption of lipid-rich fish eggs and mussel detritus is responsible for these differences. In southern Lake Michigan's Calumet Harbor (Chicago, IL, USA), round gobies have nitrogen isotope signatures with considerable spread, with some values higher than their predators and others lower than their prey. Contrary to patterns observed in linear pelagic systems, we predict that polychlorinated biphenyl (PCB) concentrations in these fish decrease with increasing size due to the lipid- and benthos-enriched diets of smaller fish. We also present here round goby PCB concentrations measured in 2005 after an invasional succession in Calumet Harbor and demonstrate how the change from one invasive mussel species to another may have led to a decrease in round goby PCB accumulation. Our results suggest that benthic-dominated systems differ from pelagic ones chiefly due to the influence of detritus and that these effects are exacerbated in systems with low species diversity and high biomass.

Keywords—Bioaccumulation Invasive Food web Great Lakes Benthic

INTRODUCTION

The North American Great Lakes have been subject to a long history of anthropogenic disturbance, including chemical contamination, habitat disruption, and proliferation of nonindigenous species [1]. The cumulative effect of these multiple, interacting pressures has been to reduce native biodiversity, resulting in food webs with trophic levels dominated by fewer, often nonnative, species. In nearshore areas of the Great Lakes, the proliferation of invasive zebra and quagga mussels (*Dreissena polymorpha* and *D. bugensis*) has led to ecosystem benthification—a shift of nutrients and energy from the water column to the sediment–water interface [2]. The resulting food webs are fundamentally different from the systems they replace, particularly in that benthic diversity is often substantially enriched relative to pelagic diversity. At the same time that the number of (native and nonnative) benthic species increases due to the enhanced habitat complexity mussel shells impart [3], the balance of species abundance is typically lost (evenness decreases). In newly invaded territories, population growth and resulting biomass of the most successful invaders can be overwhelmingly greater than those of established species, particularly during the initial proliferation stage [4]. This

is of particular concern, as species invasions are ongoing and, some have argued, accelerating [5].

In order to probe the structure and function of such highly altered food webs, we undertook a study of Calumet Harbor (Chicago, IL, USA), a nearshore system in southern Lake Michigan dominated by nonnative species. The harbor is part of the Port of Chicago, the second-largest port in the Great Lakes, and has a heavy industrial history (www.greatlakes.org/habitat/bio_recovery_report.pdf). It is located at the mouth of the Calumet River and is part of the grand Calumet area of concern, which is heavily contaminated with polyaromatic hydrocarbons, polychlorinated biphenyls (PCBs), and heavy metals (www.epa.gov/glnpo/aoc/grandcal.html).

Like much of nearshore southern Lake Michigan, Calumet Harbor's food web is categorized by relatively low species diversity [6]. Nonnative zebra mussels, quagga mussels, and round gobies constitute the majority of the harbor biomass. Though causative links remain unclear, proliferation of these invasive species has coincided with dramatic changes in the species composition of nearshore southern Lake Michigan in the latter part of the 20th century, including substantial decreases in inshore fish populations and disappearance of a major prey species, the native amphipod *Diporeia* spp. [6,7]. At the time the original data set used in the present work was collected [8], the harbor's food web contained, in addition to dreissenid mussels and round gobies, only smallmouth bass

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Table 1. Data used in food web and bioaccumulation model development

Data	Use	Reference
Stable nitrogen isotope ($\delta^{15}\text{N}$) ratios in Calumet Harbor (Chicago, IL, USA) species	Food web model development and calibration	[10] 2005 data (round gobies only): collected for present study
Round goby diet data (stomach contents)	Food web model development	[10]
Diet data for other Calumet Harbor species	Food web model development	Smallmouth bass [12,13] Crustaceans [11]
Bioenergetic parameters	Chemical uptake and loss rates for bioaccumulation	Round gobies [16] Smallmouth bass [12] Crustaceans [11]
Total polychlorinated biphenyl concentrations in Calumet Harbor species	Bioaccumulation model validation and invasional succession scenario testing	1998 and 1999 data [10] 2005 data (round gobies only): collected for present study

(*Micropterus dolomieu*, the sole top predator fish) and a small number of benthic invertebrates (primarily crayfish and amphipods). Thus, it was dominated, in terms of biomass, by invasive benthic species largely originating from the Pontocaspian region and supporting a single native predator.

We developed a model of the Calumet Harbor food web by integrating stable nitrogen isotope measurements with round goby stomach content data and literature studies of smallmouth bass and invertebrate diets [8–11]. Our model has both seasonal and ontogenetic resolution, and we focus with the greatest ecological detail on the round goby. This invasive forage fish links the previously existing Calumet Harbor food web (represented by the native smallmouth bass, which consumes round gobies) to the new and still evolving invaded food web (dominated by round gobies and dreissenid mussels, which round gobies consume).

We hypothesize that changes that have occurred in near-shore systems such as Calumet Harbor have substantial impacts on material transfer within their food webs due to new or enhanced links to the sediment–water interface. Though intimately linked to pelagic organisms and processes [12], benthic systems differ substantially from pelagic ones, in part due to the contribution of detrital materials to nutrient and energy flow. We explore such material transfer in the Calumet Harbor food web by using a fugacity-based bioaccumulation model [13] with previously published bioenergetic parameters for the harbor's species [9,10,14] to track the accumulation of PCBs in invertebrates, round gobies, and bass.

Polychlorinated biphenyls belong to the class of globally distributed persistent organic chemicals recognized as being of international concern [15], and they are important legacy contaminants in Calumet Harbor. Aquatic sediments represent some of the world's largest stores of bioaccumulative chemical contaminants [16], yet implications of the ongoing benthification of aquatic ecosystems on contaminant accumulation have not been fully explored. Understanding the behavior of contaminants in highly altered ecosystems such as Calumet Harbor can help us understand chemical dynamics and subsequent human and ecological health impacts in today's invaded landscape and in those likely to appear in the near future as a result of ongoing global change.

METHODS

Data collection

We used five classes of data to develop and calibrate a coupled food web–bioaccumulation model for Calumet Har-

bor: stable isotope data, diet information, bioenergetic rates, chemical partitioning parameters, and PCB concentrations (C_{PCB} ; Table 1). Stable isotope and PCB data for model development were from a previous study conducted between 1998 and 2000, as were round goby diet data [8]. Diet data for remaining species, bioenergetic rates, and chemical partitioning parameters were based on literature studies [9–11,14,17]. For smallmouth bass, crayfish, dreissenid mussels, and amphipods, no diet data were available for Lake Michigan. Therefore, diet studies from other systems were used as a starting point, and diets were calibrated using the Calumet Harbor isotope data (see *Supporting Information* for details; <http://dx.doi.org/10.1897/07-636.S1>).

Additional round goby C_{PCB} and stable nitrogen isotope ratios were measured for the present study in 2005 after quagga mussels largely replaced zebra mussels in the harbor. Round gobies ranging in size from 63 to 150 mm were collected via hook and line from Calumet Harbor in late August 2005. Eighteen samples were analyzed: nine composited samples of multiple fish in the medium size group (63–85 mm), and nine single-fish samples in the large size group (115–150 mm). Congener-specific C_{PCB} was measured in homogenized whole fish using soxhlet extraction with a 50:50 ratio of methylene chloride and hexane (dioxin method applied to PCBs) [18]. All concentrations were measured in duplicate and surrogate-adjusted (see *Supporting Information*; <http://dx.doi.org/10.1897/07-636.S1>). Lipid content was measured via gravimetric analysis [19]. Stable nitrogen and carbon isotopes ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) were measured in round goby samples with an isotope ratio mass spectrometer.

Stable isotope analysis

The baseline structure for development of our Calumet Harbor food web model was based on literature diet information for each of the harbor's species. The food web included, from highest to lowest trophic level: smallmouth bass consuming crayfish and round gobies; round gobies consuming zebra mussels and amphipods; crayfish consuming invertebrates and primary producers; amphipods and zebra mussels consuming primary producers; and primary producers (phytoplankton and periphyton). We used $\delta^{15}\text{N}$ ratios to gain insight into how this assumed structure differed from actual predator–prey relationships in Calumet Harbor. Nitrogen isotope analysis is widely employed in food web studies as a continuous measure of trophic position, as the $\delta^{15}\text{N}$ ratio increases by approximately 3.4‰ from prey to predator [20]. To compare our baseline

model with the Calumet Harbor food web, we constructed its isotope profile using a mixing model:

$$\delta^{15}\text{N}_i = \sum w_{i,j}(\delta^{15}\text{N}_j + 3.4) \quad (1)$$

where $\delta^{15}\text{N}_i$ is the isotopic signature of organism i , $w_{i,j}$ is the proportion of prey j in i 's diet, and $\delta^{15}\text{N}_j$ is the isotopic signature of organism j . As is typically done, we assumed an elevation of 3.4‰ in the isotope ratio of a predator relative to its prey and summed these contributions over all n prey [12]. The trophic position, P_i , of each species was then defined relative to a baseline species as follows:

$$P_i = \frac{\delta^{15}\text{N}_i - \delta^{15}\text{N}_0}{3.4} + P_0 \quad (2)$$

where P_0 is the trophic position delegated to the baseline species, $\delta^{15}\text{N}_i$ is the stable nitrogen isotope ratio of species i , $\delta^{15}\text{N}_0$ is the nitrogen isotope ratio of the baseline species, and the prey-to-predator fractionation factor is 3.4‰. We designated the zebra mussel as the baseline species at trophic position 2, because isotope fractionation in primary consumers tends to be less seasonally variable than in primary producers [21].

The baseline food web's isotope profile was then compared with the actual profile as measured in the 1998 and 1999 set of $\delta^{15}\text{N}$ data for the species in Calumet Harbor [8].

Our initial structure was iteratively updated using round goby stomach contents data, additional literature resources, and the isotope turnover model described in the next section to reflect a food web structure leading to the actual trophic profile measured in the harbor.

Isotope turnover model

We hypothesized that both seasonal changes in diet and consumption of detritus were important to material cycling in the Calumet Harbor food web, but both are highly variable and both occur on short time scales not reflected in steady-state isotope mixing or bioaccumulation models. We therefore constructed a tissue turnover model to probe the consequences of temporary diet changes on species' effective trophic positions. This model allowed us to estimate the consumption rate of a seasonally available diet item for use in the bioaccumulation model, which is based on a steady-state snapshot picture of food web structure.

The model is controlled by three parameters. Egg consumption is characterized by a Poisson process with average rate r , such that the number of egg meals during spawning season ($N(t)$) is given by the Poisson distribution:

$$P\{N(t) = n\} = \frac{(rt)^n}{n!} e^{-rt} \quad (3)$$

where P is the probability that n consumption events occur during time interval t , given an average consumption rate r . Using this Poisson process, we capture both the frequency of consumption and the stochastic nature of prey choice in varied diets. The step size, s , determines the increase in isotope signature resulting from one instance of consumption. If an instance of uptake occurs at time t_i , the $\delta^{15}\text{N}$ signature is elevated by a constant value, s , above the value at the previous time step, t_{i-1} :

$$\text{Uptake: } \delta^{15}\text{N}(t_i) = \delta^{15}\text{N}(t_{i-1}) + s \quad (4)$$

Finally, the characteristic turnover time, τ , determines the rate of isotope turnover after consumption. The rate of turnover at time t_i is based on the $\delta^{15}\text{N}$ signature at initial time t_0 and on τ :

$$\text{Turnover: } \delta^{15}\text{N}(t_i) = \delta^{15}\text{N}(t_0) e^{-(t_i-t_0)/\tau} \quad (5)$$

Though relatively few studies have been made on stable isotope turnover in aquatic organisms, the turnover time for $\delta^{15}\text{N}$ in fast-growing fish such as the round goby is known to be on the order of months [22]. We used this value for τ to find the step size s leading to an expected change in the equilibrium $\delta^{15}\text{N}$ signature following a diet switch simulation.

This procedure allowed us to estimate r , the average rate of consumption of the diet item in question, by fitting the distribution of $\delta^{15}\text{N}$ values predicted by the model to those observed in Calumet Harbor. Our turnover model thus allowed direct visualization of the time-dependent effect of diet changes on species' effective trophic positions, at the same time providing the means to incorporate such changes into a steady-state bioaccumulation model through the estimation of r .

Bioaccumulation model

We used the fugacity-based bioaccumulation model developed by Sharpe and Mackay [13] to quantify the effect of using increased ecological detail on predictions of chemical transfer. We produced predictions of total, lipid-normalized C_{PCB} in Calumet Harbor species using two food web models: the detailed food web model described earlier and the baseline model developed prior to the isotope analysis, which integrated a species' diet over all life stages to create a single, averaged diet and ignored consumption of detritus and seasonal diet changes (see *Supporting Information*; <http://dx.doi.org/10.1897/07-636.S1>). Previously published bioenergetics models linked these food web structures and the bioaccumulation model by providing chemical uptake and loss rates via consumption, respiration, and egestion [9,10,14].

We compared model predictions to 1998 and 1999 C_{PCB} measurements from Calumet Harbor [8]. In addition, C_{PCB} data collected in 2005 were used to support the 1998 and 1999 predictions and to illustrate the use of the coupled food web bioaccumulation model in scenario testing by exploring possible PCB bioaccumulation consequences associated with the change in dominance from zebra to quagga mussels that occurred in the harbor between 1999 and 2005.

RESULTS AND DISCUSSION

Calumet Harbor trophic position profile

Despite Calumet Harbor's apparently simple trophic structure (few species), we find it has a surprisingly variable nitrogen isotope profile, which cannot be explained by analytical error (as designated by error bars, Fig. 1). Primary producers are expected to be at trophic position 1, at the base of the food web. Yet in Calumet Harbor, the effective trophic position (P ; we use the term effective trophic position rather than trophic level because we analyze materials such as detritus, which, being neither producers nor consumers, do not belong to a trophic level in the traditional sense) of primary producers ranges between 1 and 2.8. As in most aquatic ecosystems, primary producer trophic position in the harbor is calculated from $\delta^{15}\text{N}$ ratios measured in filtered algae samples, which cannot be separated from associated detritus. Variability in primary producer signatures is often attributed to the presence of such detritus [23], which plays an important role in aquatic ecosystems. Round gobies and zebra mussels are expected to contribute the major proportion of autochthonous detritus, as they are the most abundant species in the harbor by biomass. Given that the sampling dates (September 23, 1998, and July

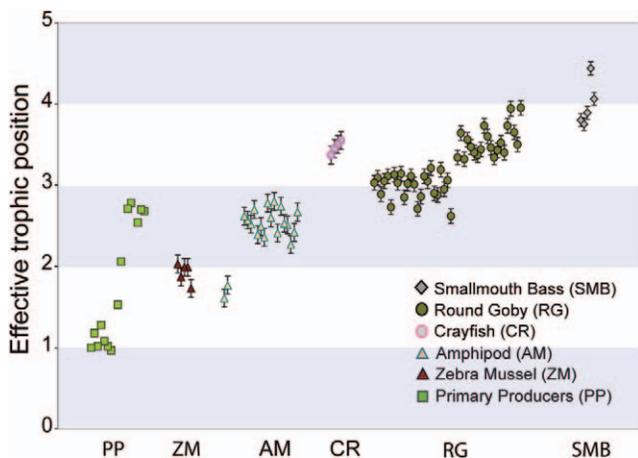


Fig. 1. Effective trophic position of Calumet Harbor (Chicago, IL, USA) species. Error bars represent analytical error (standard deviation of measurement of $\delta^{15}\text{N}$, carried through to trophic position). Analytical error for primary producers is not available but is expected to be consistent with the values for other Calumet Harbor species.

29, 1999) fell during round goby spawning season (May–August), round goby eggs would have been an abundant lipid-rich food source for small round gobies. Higher-trophic-position smallmouth bass eggs would not have been available, however, as they spawn in southern Lake Michigan during June.

Zebra mussels contribute year-round to the harbor's detritus through their feces and pseudofeces. We assumed that fish eggs, as well as the carcasses of postspawn males that would also have been abundant after spawning season, have nitrogen isotope signatures similar to their source species (forage fish at $P \approx 3$). The isotopic signature of zebra mussel waste derives from a mixture of feces and pseudofeces; mussel feces reflect the isotopic composition of their diet (primary producers at $P = 1$), while pseudofeces contain rejected particles (which in Calumet Harbor presumably include particles found in seston that do not contribute to the mussel diet, which, as shown, have trophic positions ranging from $P \approx 1$ to $P \approx 3$). This will lead to a trophic position of mussel detritus of $P \approx 2$, depending on the relative contributions of feces and pseudofeces. These values, together with the true primary producer signature at $P = 1$, encompass the range in P observed at the base of Calumet Harbor's food web.

An elevated isotopic signal, likely reflecting consumption of detritus, is most evident in amphipods and round gobies (Fig. 1). Crayfish trophic position, though elevated, is not highly variable. Amphipods, on the other hand, appear to form two distinct groups, one at $P = 1.5$ and the other with $2 \leq P \leq 3$. Round goby P ranges from as low as 2.5 to as high as 4. The range in smallmouth bass P is consistent with consumption of crayfish and round gobies, given the P value of these prey species.

A number of studies stress the importance of within-species variability in trophic position and the need for greater resolution in the lower trophic levels to account for seasonality, ontogeny, and omnivory [20,24]. Round gobies and amphipods are good candidates for this type of analysis, as their diets display all three of these features: round gobies consume seasonally available smallmouth bass and round goby eggs and transition from consuming amphipods to zebra mussels as they grow, while amphipods are opportunistic feeders often occu-

pying a continuum of trophic positions, rather than a single, well-defined trophic level [25].

In Calumet Harbor, the amphipod community is dominated by *Gammarus fasciatus*, an invertebrate that is often associated with dreissenid mussels and is known to consume mussel feces and pseudofeces. The consumption of detritus at $P = 2$ would elevate amphipods to $P \approx 3$. Though elevation of amphipod $\delta^{15}\text{N}$ has been attributed to either consumption of detritus or carnivory [26], the low diversity of Calumet Harbor's food web suggests that generalist amphipods not restricted to consuming plankton would rely on the most abundant sources of nutrition, zebra mussel detritus at $P = 2$, thus elevating their trophic position to $P = 3$.

We use two additional independent analyses to complement the $\delta^{15}\text{N}$ data and quantify the elevation of species' effective trophic position due to consumption of detritus: Round goby stomach contents data, which enable us to develop a model for the round goby diet as a function of length, and an isotope turnover model, which estimates tissue turnover following temporary diet changes. In the latter analysis, the distribution of P in round gobies and amphipods, together with sampling date (season), is used to estimate an annual average consumption rate of fish eggs and zebra mussel detritus, respectively.

Round goby ontogenetic diet changes

Like many fish species, round gobies undergo ontogenetic diet changes. Previous studies of stage-structured populations have focused primarily on piscivorous fish (for example, yellow perch [27]), whose diets may span several trophic levels, transitioning from consuming plankton ($P = 1$) to consuming invertebrates ($P = 2$) and to consuming fish ($P = 3$). Round goby stomach contents reveal a subtler ontogeny: Small gobies (<70 mm in length) consume nonmussel invertebrates (primarily amphipods); medium-sized gobies (70–100 mm in length) consume a mixed diet of amphipods and zebra mussels; and large gobies (>100 mm) consume zebra mussels exclusively. Though round gobies remain invertivores throughout their life span, their population can nevertheless be represented by three states. The Calumet Harbor stable isotope data suggest that each state has a distinct trophic position resulting from a size-dependent diet.

Smallmouth bass also have stage-structured life histories; though we do not have stomach contents data for this species, we know from the literature that they transition from consuming primarily invertebrate prey to consuming crayfish and fish [28].

Isotope turnover model

Seasonal diet components are not readily observable in stomach contents, which give only a snapshot of an organism's diet that is specific to the sampling date. Fish eggs, for example, are a key feature of the round goby diet [29] but are present for only a fraction of the year. Thus, they are unlikely to be found in stomach contents but make a substantial contribution to effective trophic level due to their high-trophic-position origins. Consumption of eggs between May and August boosts round goby trophic position from $P = 3$ to $P = 4$, after which it returns to a baseline value consistent with its size-based invertebrate diet over some characteristic turnover time, τ . In our modeling, we set $\tau = 1$ month. Field observations suggest that smaller round gobies are more likely to prey on fish eggs because the nest defense behavior of the

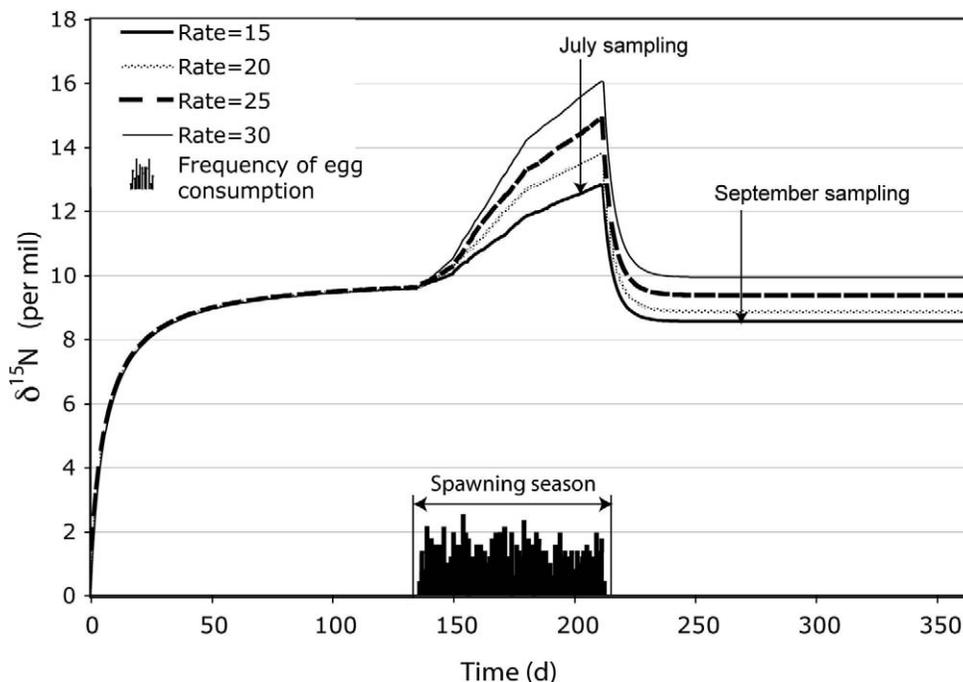


Fig. 2. Isotope turnover model. During spawning season, consumption of eggs is drawn from a Poisson distribution based on consumption rate (black bars). Round goby isotope signature ($\delta^{15}\text{N}$, per mil: parts per thousand) reaches an equilibrium value (consuming a diet of amphipods) and then rises during spawning season when consuming fish eggs. After spawning season, $\delta^{15}\text{N}$ regains the equilibrium value with characteristic time, τ . The consumption rate affects $\delta^{15}\text{N}$ at sampling dates (September 23, 1998, and July 29, 1999, indicated by arrows). We fit the distribution of $\delta^{15}\text{N}$ values associated with different consumption rates (solid and dashed lines) to actual $\delta^{15}\text{N}$ distributions from September 23, 1998, and July 29, 1999, measurements to estimate the average consumption rate of this seasonal diet item over the year for use in a steady-state bioaccumulation model [13].

smallmouth bass is more likely to be triggered by larger round gobies. Round gobies have also been found to defend their nests against other round gobies [30]. Our model therefore restricts opportunistic consumption of round goby and bass eggs to the smallest size class of round goby during spawning season.

In order to determine the contribution of egg consumption to the round goby diet as integrated over the year, we modeled instances of egg consumption during the spawning season (May–August) using a Poisson process. The stochasticity of egg consumption described in this way allows us to model the variability seen in the samples.

The turnover model generates an $\delta^{15}\text{N}$ profile for the year given this particular consumption pattern of food with elevated $\delta^{15}\text{N}$ signatures (Fig. 2). We can then estimate the average rate of consumption over the year by generating a large set of isotope profiles and fitting the distribution of trophic positions predicted to the actual 1998 and 1999 data at the given sampling dates (September 23, 1998, and July 29, 1999).

Our results show how elevation of the round goby trophic position extends beyond the spawning season due to the long turnover time, τ . The turnover model illustrates how the sampling date, particularly when considering seasonal diets, has a large effect on measured $\delta^{15}\text{N}$ levels and highlights the need to integrate stable isotope measurements with other sources of food web data, such as stomach contents and field observations. Even species without seasonally variable diets are affected by the cascading effects of the seasonal diets of their prey.

Food web model

The inclusion of seasonal and ontogenetic details and consumption of detritus dramatically alters Calumet Harbor's tro-

phic description (Fig. 3). The initial baseline food web we used to assess the isotope data (Fig. 3a) differs substantially from our final model, which includes size-dependent trophic relationships (round goby stage structure) and consumption of detritus characterized as year-round (amphipods), seasonal (round gobies), and size dependent (round gobies). Links to higher-trophic-position species through consumption of eggs and detritus cause a positive feedback effect on nutrient and energy cycling.

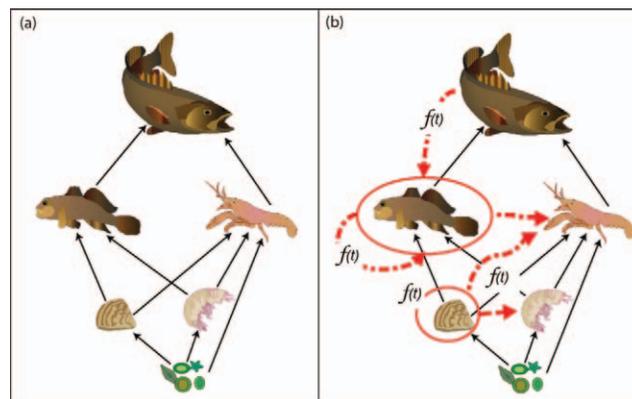


Fig. 3. Calumet Harbor (Chicago, IL, USA) food web model. (a) Simple trophic description showing predator–prey links. (b) Model integrating time-dependent effects (ontogeny and seasonality) and consumption of detritus. Trophic links for the round goby and smallmouth bass are functions of time, $f(t)$, as size changes (ontogeny). Trophic links for crayfish and round gobies are a function of time, $f(t)$, through seasonal availability. Consumption of detritus and fish eggs links predators to prey items at equal or higher trophic positions than their own, creating a positive feedback effect (dashed lines).

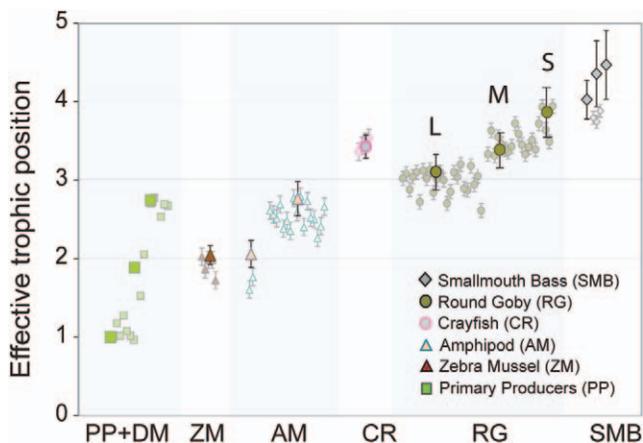


Fig. 4. Trophic position profile as predicted by the full seasonal, stage-structured food web model (dark symbols) superimposed over Calumet Harbor (Chicago, IL, USA) data (faded symbols). Error bars indicate the range of predicted values as determined by the isotope turnover model, and round goby populations are separated into small (S), medium (M), and large (L). Primary producers and detrital materials (DM) are both included.

Predicted trophic position profile (1998 and 1999)

Using our seasonally resolved, stage-structured food web description (Fig. 3b), we can now capture the important features of the empirical trophic position profile of Calumet Harbor, including the range of trophic positions attributed to primary producers, the separation of amphipods into two distinct trophic groups, and the range in round goby trophic positions (Fig. 4). Within-population trophic variability is illustrated by the error bars, which indicate the range of values that result from multiple runs of the turnover model for amphipods and small round gobies. This variability is then transferred via trophic relationships to the remaining members of the Calumet Harbor food web. The turnover model was used to predict the isotope profile in small round gobies given two sampling dates representative of the 1998 and 1999 data set: Midsummer, when eggs would have been available, and early fall, after the end of spawning season.

The most surprising prediction of our food web model concerns round goby ontogeny: The smallest size class has the highest effective trophic position due to consumption of detritivorous amphipods and fish eggs, whereas the largest size class, which consumes only zebra mussels, is at the lowest trophic position. This nutritional recycling has important implications for contaminant transfer.

PCB bioaccumulation (1998 and 1999)

In order to assess the effect of ecological detail on predictions of chemical transfer, and probe the positive feedback effect of detritus on PCB bioaccumulation, we compared measured concentrations in Calumet Harbor organisms to predictions made using two trophic structures. First, we used our baseline model (Fig. 3a), which excludes detritus and fish eggs and integrates diets across all round goby and bass stages into a single average diet for each species. Second, we used our seasonal, stage-structured model (Fig. 3b). The baseline model contains six species: Primary producers, amphipods, zebra mussels, crayfish, round gobies, and smallmouth bass. Our full model, on the other hand, resolves round gobies and smallmouth bass into three stages (small, medium, and large) and includes round goby eggs, smallmouth bass eggs, and zebra

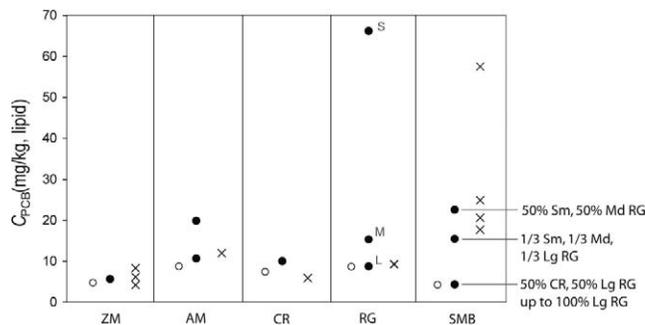


Fig. 5. Polychlorinated biphenyl concentration (C_{PCB}) predicted by baseline model (\circ , no detritus, averaged adult diet), predicted by full model (\bullet , including seasonality, ontogeny, and detritivory), and measured in Calumet Harbor (\times , Chicago, IL, USA) species [8]. The effect of consuming highly contaminated small round gobies is illustrated by full model predictions of smallmouth bass C_{PCB} . ZM = zebra mussel; AM = amphipod (herbivorous or detritivorous); CR = crayfish; RG = round gobies (small, medium, and large); SMB = smallmouth bass (small, medium, and large).

mussel feces and pseudofeces in species' diets (see *Supporting Information* for link strengths in each food web; <http://dx.doi.org/10.1897/07-636.S1>).

The 1998 and 1999 Calumet Harbor data set [8] includes measurements of C_{PCB} in 10 samples: Three composite zebra mussel samples (14–22 g total wt each), one composite amphipod sample, one composite crayfish sample ($n = 10$), two composite round goby samples falling in the medium-to-large size range ($n = 8$, total length [TL] = 82–127 mm; $n = 7$, TL = 77–92 mm), and three smallmouth bass samples ($n = 2$, TL = 415–425 mm; $n = 3$, TL = 380–390 mm; $n = 3$, TL = 335–355 mm). We compare C_{PCB} measured in these samples to predictions of the baseline and full models (Fig. 5).

The models are equally successful in predicting C_{PCB} in lower-trophic-position species (zebra mussels and amphipods). Both models slightly overpredict C_{PCB} in crayfish, possibly due to the bioenergetic parameters used. Indeed, similar overpredictions were observed in Morrison et al.'s original work, which nonetheless remains one of the few studies that has compiled macroinvertebrate bioenergetic parameters [9].

It is in the bioaccumulation predictions for the higher-trophic-position species where differences in the food web models become pronounced. In the three round goby size classes considered by the full model, predicted C_{PCB} decreases with increasing size, a trend that follows exactly the relationship between trophic position and size. Recycled contaminants are introduced to the round goby population via two routes: indirectly through consumption of detritivorous amphipods and directly through consumption of fish eggs (Figs. 3a and 5). These diet items set up contaminant feedback loops that amplify the accumulation of PCBs. Even though egg consumption constitutes only 16% of the small round goby diet over the year (as estimated through our isotope turnover model), it results in the highest C_{PCB} occurring in the youngest gobies. Medium-sized round gobies, which feed on zebra mussels in addition to amphipods, have a lower C_{PCB} , and large round gobies, which feed exclusively on zebra mussels, have the lowest C_{PCB} . Similar ontogenetic trends are predicted for smallmouth bass, but given its long lifetime and diet dominated by fish, C_{PCB} variation with size spans a narrower range.

The predictions of the bioaccumulation model are particularly dramatic for smallmouth bass. Based on smallmouth

bass bioenergetics [10], our model predictions indicate that smallmouth bass do not biomagnify relative to the round goby. If we look only at the PCB data for the harbor, where large round gobies and smallmouth bass were collected, it appears that there is biomagnification, but this conclusion is not supported by the bioaccumulation model unless there is substantial error in the bioenergetics model used to calculate uptake and loss rates [10]. The baseline model, which includes consumption of only large round gobies and crayfish, substantially underpredicts smallmouth bass C_{PCB} .

It is only by including smaller, more contaminated round gobies in the smallmouth bass diet that we are able to accurately predict smallmouth bass C_{PCB} in the harbor. In the smallmouth bass panel of Figure 5, we demonstrate the effect of consuming these more contaminated smaller fish. The lowest prediction of the full model is obtained when smallmouth bass consume only crayfish, only large round gobies, or any combination of these two prey species (note that this is equivalent to the prediction of the baseline model). The next-higher prediction of smallmouth bass C_{PCB} is based on a diet consisting of small, medium, and large round gobies in equal parts. Finally, the highest full model prediction, which is close to the actual values measured in smallmouth bass, is achieved using a diet that consists of 50% medium and 50% small round gobies.

Using our more complete trophic understanding, we find a very different and unexpected outcome—given the structure of the Calumet Harbor food web as developed through stable isotope and diet analysis, only consumption of highly contaminated small round gobies can explain the observed pattern of C_{PCB} in smallmouth bass. This implies that the apparent biomagnification from round goby to smallmouth bass in the 1998 and 1999 data is misleading, as it is not based on the bass's true diet.

Our predictions of C_{PCB} in large round gobies are in good agreement with the data. Furthermore, this bioaccumulation trend is supported by results from studies in a number of benthic-dominated systems. In a Labrador food web, Kuzyk et al. found shorthorn sculpins (*Myoxocephalus scorpius*), benthic fish similar to round gobies, showed only a weak tendency for C_{PCB} to increase with length in males, and found a decrease in C_{PCB} with length for females [31]. Martin and coworkers found that slimy sculpin (*Cottus cognatus*) in Lake Ontario were more contaminated with perfluoroalkyl compounds than lake trout from the same food web [32]. In Lake Erie, Barton et al. found that trophic position for nearshore round goby populations did not increase with size, and larger values were found in smaller round gobies [33]. In one recent study of Lake Erie, where magnification of PCBs from round gobies to smallmouth bass was apparently observed, round gobies collected ranged in size from 70 to 140 mm (medium to large) [34]. In our own predictions, comparisons of large round goby C_{PCB} and smallmouth bass C_{PCB} also seem to indicate biomagnification is occurring, but bioenergetic modeling suggests that the high C_{PCB} in smallmouth bass in fact comes from consumption of smaller round gobies.

In order to better validate these findings, we collected additional data in Calumet Harbor in 2005. The 1998 and 1999 Calumet data were not collected with the aim of identifying ontogenetic differences in smallmouth bass and round gobies and did not provide direct evidence for this unexpected trend. Only medium-to-large specimens of each fish were collected, and without enough samples of each size class or sample rep-

Table 2. Round goby polychlorinated biphenyl concentration (C_{PCB}) and stable isotope ratios (per mil: parts per thousand) in Calumet Harbor (Chicago, IL, USA), 2005

Length (mm)	Size class	$\delta^{15}\text{N}$ (per mil)	C_{PCB} (mg/kg, lipid normalized)	Average C_{PCB}
63–66	Medium	10.404	2.64	
67–69	Medium	9.697	2.33	
70–71	Medium	9.962	2.72	
72–73	Medium	10.711	2.61	
75	Medium	10.788	2.41	
77–78	Medium	10.352	3.48	Medium, 2005
79–80	Medium	10.030	2.63	2.72 (0.35) ^a
81–82	Medium	10.551	2.63	
83–85	Medium	10.458	3.09	Large, 2005
115	Large	10.643	3.00	2.44 (0.73)
117	Large	10.656	3.36	
119	Large	10.756	2.55	Large, 1998 and 1999
122	Large	10.615	1.47	9.2 (0.07) ^b
122	Large	10.164	3.47	
133	Large	11.058	1.77	
135	Large	10.640	1.66	
139	Large	10.245	2.47	
150	Large	10.859	2.24	

^a Values in parentheses are standard deviations.

^b For 1998 and 1999 data, only two data points were available.

licates, measures of variability and analytical uncertainty are not available to validate the significance of our model results. However, in the intervening time between collection of the original data set and 2005 sampling, we found that an ecological succession had occurred, changing both the biotic and the bioaccumulation characteristics of the system.

PCB bioaccumulation following invasional succession

In August 2005, 18 additional round goby samples were collected for congener-specific C_{PCB} measurements. These round gobies ranged in size from 60 to 104 mm. No small round gobies (<60 mm) were caught. The C_{PCB} was highly variable, such that a statistically significant decrease with size was not found. In addition, there was an observed lack of larger males in the sample, highlighting the strong influence of seasonal effects. August represents the end of the round goby spawning season, when many postspawning males have died, and the remaining population is a mix of pre- and post-maturity females and younger males with varying diets, lipid levels, and consequently, C_{PCB} . Most surprisingly, C_{PCB} measured in these round gobies was on average three times lower than in samples from the 1998 and 1999 data set (Table 2).

Despite high variability and lower relative C_{PCB} , the 2005 data confirm the lack of an increasing trend in round goby contamination with size, particularly if we contrast patterns typical of pelagic fish such as alewives (*Alosa pseudoharengus*), trout, or salmon [35,36] with observations from the harbor. It is clear that there is not a significant increase in round goby C_{PCB} with size, and similar observations in other systems discussed earlier suggest that this lack of trend is in fact a signature of benthic, as opposed to pelagic, systems [31–33]. Furthermore, the effects of ontogenetic shifts and use of detrital resources on PCB accumulation, key features of our model, can help explain the large observed variability. If we assume that much of the variability in the data results from varying consumption levels of detritus or fish eggs, and include

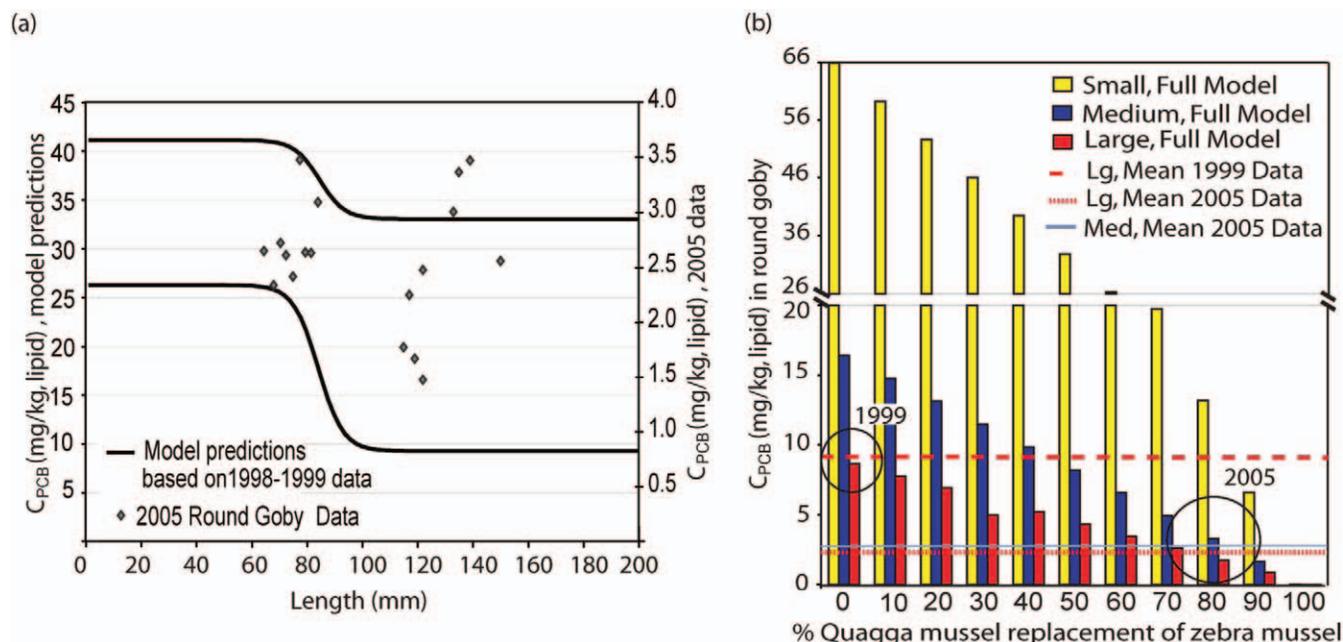


Fig. 6. Bioaccumulation trends in Calumet Harbor (Chicago, IL, USA) following the zebra-to-quagga mussel succession. (a) Polychlorinated biphenyl concentration (C_{PCB}) in round gobies collected in 2005, and model predictions from 1998 to 1999. Model prediction range (solid black lines) is based on two assumptions: Either no round gobies eat eggs, or all gobies eat eggs at the rate estimated for small round gobies in the 1998 and 1999 data set (16%). In either case, the round goby diet changes as a function of size (switches from amphipods to zebra mussels). (b) Zebra-to-quagga mussel succession. This simulation illustrates how a species invasion could explain the drop in C_{PCB} in large (red column), medium (blue column), and small (yellow column) round gobies. Measured C_{PCB} in large round gobies in 1999 (red dashed line) corresponds to 0% quagga mussel replacement. Range of C_{PCB} in medium (mean, blue solid line) and large (mean, red dotted line) 2005 round gobies corresponds to 80% succession. This is in good agreement with recent observations in the area.

the shift in PCB uptake that results from diet shifts in the round goby, we can bracket the relative range of observed C_{PCB} from medium to large fish quite well. We assume two extreme cases for egg consumption throughout round goby ontogeny: At the low end no round gobies consume eggs, whereas at the high end all round gobies consume the amount (16%) predicted by the isotope turnover model only for the small round gobies (Fig. 6a). Increased reliance on detrital resources can lead to unexpected accumulation patterns, including a reversal of the increase in trophic position and C_{PCB} we expect with increasing species size in linear, pelagic systems. This is not entirely surprising given the different nature of benthic food webs and the recycling of resources that occurs there, as shown in Figure 3a. It appears, in fact, to be a signature of benthic systems. Given the continued expansion of species like the zebra and quagga mussel and the round goby worldwide, our results imply that a better understanding of detailed consumption patterns is necessary to understand risk from contaminant transfer in benthified aquatic systems.

However, explaining the large drop observed in C_{PCB} between 1999 and 2005 remains problematic. This decrease did not coincide with any dredging activity in the sampling area or with natural weathering of PCBs (K_{OW} is high, and weathering of highly chlorinated PCBs could not occur in such a short time). The only major ecological change that occurred in Calumet Harbor during this time was a shift in dominance from zebra mussels to quagga mussels. How might this ecological shift have led to a decrease in round goby C_{PCB} ? The simplest explanation is that quagga mussels are somehow less contaminated than zebra mussels. Indeed, some studies have shown that zebra and quagga mussels can accumulate contaminants differently, though these studies have largely been restricted to metals or have failed to show consistent trends

between or among systems [37–39]. There is some physiological basis for this difference, as quagga mussels tend to preferentially allocate energy to growth and are more efficient in their energy use while zebra mussels allocate more energy to reproduction [40]. However, we hypothesize that much of the observed difference is likely due to spatial heterogeneity and microhabitat use.

Quagga and zebra mussels are trophically identical—they filter at similar rates, have similar diets, and are consumed by the same species (round gobies). The only major difference in their ecology is in their habitat preference: Quagga mussels can colonize sandy and unconsolidated substrates at deeper depths; zebra mussels attach to hard surfaces and are limited to shallow waters. In Calumet Harbor, periphyton (the complex matrix of algae and heterotrophic bacteria attached to submerged surfaces in aquatic environments) is concentrated on stable, rocky substrates. This matrix has been shown to substantially bioaccumulate contaminants [41]. Sandy substrates in the area, on the other hand, have nondetectable levels of PCBs (K. Mrozek, U.S. Army Corps of Engineers, Chicago, IL, personal communication). It is therefore possible that in Calumet Harbor zebra mussels, which tend to be closely associated with periphyton, are more contaminated, while quagga mussels subsisting on low-organic-content sandy substrates provide a relatively clean food source for the round goby.

We therefore constructed a simulation using our coupled food web–bioaccumulation model that explores the zebra mussel–quagga mussel succession in Calumet Harbor and its effects on PCB accumulation, assuming that quagga mussels are a clean food source. Starting in 1999 with 100% zebra mussels, we gradually replace zebra mussels and their pseudofeces with quagga mussels and their pseudofeces in each species' diet, increasing the relative proportion to 100% quagga (Fig. 6b).

Quagga mussel feces and pseudofeces are also modeled as clean (no PCBs) to explore possible consequences of such a diet change to the harbor's detritivores and to the bioaccumulation feedback effect of detritus consumption.

The round gobies sampled in 2005 ranged in size from 63 to 150 mm, corresponding to the medium and large size classes. We found that the range of PCB values measured in these fish is consistent with our predictions for the medium and large gobies given a quagga mussel succession of 70 to 80% (Fig. 6b), a value also consistent with current observations of quagga populations in the area (T.F. Nalepa, National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, MI, USA, personal communication; D.J. Jude, unpublished data). This illustrates how, knowing the contaminant accumulation potential in a newly introduced prey species, we could use our model to either estimate a succession rate given concentrations in predator species or predict the effect of an invader on contaminant fate. Note that predicted C_{PCB} decreases more rapidly in small round gobies than in large ones, illustrating the feedback effect of contaminant cycling through consumption of fish eggs and detritivorous amphipods.

Though inconvenient to our original intent, the quagga mussel succession is an apt illustration of the constantly shifting nature of aquatic ecosystems under anthropogenic influence, and it provides us with the opportunity to test our modeling approach in a unique manner. The different rates at which species and size classes of species are affected by an assumed decrease in contaminant uptake (consumption of clean food) also provide additional evidence of the impact of including greater ecological resolution in bioaccumulation models. This modeling exercise demonstrates the utility of our coupled food web–bioaccumulation modeling approach as a tool for scenario testing.

CONCLUSION

The transfer of PCBs from round gobies to smallmouth bass has important implications for restoration initiatives, as well as those activities targeted at protecting smallmouth bass, an important sport fish in the United States. In our model, young round gobies constituted between 20 and 40% of the smallmouth bass diet. However, studies of smallmouth bass populations following round goby invasion have found that bass are switching to piscivory earlier, as round goby populations provide an abundant new food source [11]. This may mean that highly contaminated younger round gobies are becoming a larger fraction of their diet as smallmouth bass begin consuming fish earlier in their life cycle. Furthermore, the contaminant feedback loops that raise round goby C_{PCB} above what would be expected, given their assumed forage fish trophic position ($P = 3$), suggest that more stringent sediment cleanup targets would be necessary to provide protection for smallmouth bass and their eventual predators, humans.

More broadly, results from Calumet Harbor provide insight into widespread ecosystem trends. Much of the influence detritus exerts on nutrient, energy, and contaminant cycling in Calumet Harbor may be amplified by the lack of diversity, and related high exotic organism biomass, that has resulted from multiple ecosystem stresses present in this highly altered Great Lakes ecosystem. Without a diverse set of species at each trophic level to dilute recycling effects, ecosystem resources and their associated contaminants are funneled through a single set of links that place top predators—including humans—at

greater risk. Based on our modeling results, the Ponto-Caspian invasions occurring worldwide are not only responsible for a reduction in biodiversity but also catalyzing changing patterns for contaminant transfer and risk. This is of particular concern given the persistence of such chemicals and growing evidence of their negative effects on human health, even at very low concentrations. Given the continued evolution of aquatic food webs subject to species invasions and, in the near future, the unfolding trends of climate change, we may expect to see further unexpected changes to the level of health risk to human and wildlife populations from these widespread and persistent contaminants.

SUPPORTING INFORMATION

Table S1. Food web matrices for baseline and full food web models.

Table S2. Bioaccumulation parameters used.

Table S3. Characteristics of polychlorinated biphenyl (PCB) congeners measured in Calumet Harbor round gobies.

Table S4. Biomagnification (BMF) matrices and bioconcentration vectors for baseline and full food webs.

Figure S1. Round goby stomach contents as a function of size. Small round gobies (<70 mm) consume benthic invertebrates (primarily amphipods), medium gobies (70–100 mm) consume both amphipods and zebra mussels, and large gobies (>100 mm) consume zebra mussels exclusively. These data are based on a 1998 and 1999 study of the harbor [7].

Figure S2. Comparison of congener-specific polychlorinated biphenyl (PCB) concentrations between duplicate measurements of 2005 round goby samples. Perfect agreement is shown by a solid line, symbols represent individual samples. The presence of only small deviations from the line indicates that analytical uncertainty is low.

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