

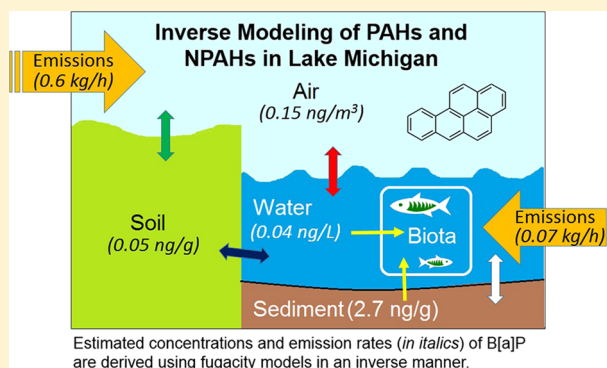
Multimedia Model for Polycyclic Aromatic Hydrocarbons (PAHs) and Nitro-PAHs in Lake Michigan

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Supporting Information

ABSTRACT: Polycyclic aromatic hydrocarbon (PAH) contamination in the U.S. Great Lakes has long been of concern, but information regarding the current sources, distribution, and fate of PAH contamination is lacking, and very little information exists for the potentially more toxic nitro-derivatives of PAHs (NPAHs). This study uses fugacity, food web, and Monte Carlo models to examine 16 PAHs and five NPAHs in Lake Michigan, and to derive PAH and NPAH emission estimates. Good agreement was found between predicted and measured PAH concentrations in air, but concentrations in water and sediment were generally under-predicted, possibly due to incorrect parameter estimates for degradation rates, discharges to water, or inputs from tributaries. The food web model matched measurements of heavier PAHs (≥ 5 rings) in lake trout, but lighter PAHs (≤ 4 rings) were overpredicted, possibly due to overestimates of metabolic half-lives or gut/gill absorption efficiencies. Derived PAH emission rates peaked in the 1950s, and rates now approach those in the mid-19th century. The derived emission rates far exceed those in the source inventories, suggesting the need to reconcile differences and reduce uncertainties. Although additional measurements and physiochemical data are needed to reduce uncertainties and for validation purposes, the models illustrate the behavior of PAHs and NPAHs in Lake Michigan, and they provide useful and potentially diagnostic estimates of emission rates.



INTRODUCTION

In the atmosphere, polycyclic aromatic hydrocarbons (PAHs) are widely distributed and persistent pollutants that are released mainly through incomplete combustion.¹ In aquatic environments, PAHs arise from atmospheric deposition, urban runoff, municipal or industrial effluents, and petroleum spills.² Some PAH compounds are carcinogenic to humans and fish.^{3–5} Nitro-PAHs (NPAHs), which are nitro-derivatives of PAHs, also are widely distributed in the environment, and result from both primary emissions from combustion sources and atmospheric transformations of PAHs.^{6,7} Although environmental concentrations are far lower than those of the parent PAHs,^{8,9} NPAHs can have stronger carcinogenic and mutagenic activity.¹⁰

PAH contamination in the U.S. Great Lakes has been of concern for decades¹¹ due to the lakes' large surface areas,¹² long hydrologic retention times and great depths,¹³ the many urban and industrial sources surrounding the lakes, and the presence of Areas of Concern and other contaminated sites. Historically, Lake Michigan has received large inputs of PAHs from the urban and industrial centers surrounding its southern portion.² Airborne PAH levels have been monitored since 1990 by the Integrated Atmospheric Deposition Network (IADN),¹⁴ and sediment measurements have been performed intermittently (in 1982, 1986, 1993, 1996, 1998, 2001, and

2011).^{2,15–19} Surface water measurements of PAHs were reported in one study in 2000.²⁰ There have been few PAH measurements in aquatic biota of Lake Michigan.^{21–24} Because of the "biodilution" seen in marine organisms (a result of rapid biotransformation at high trophic levels),^{25,26} PAH concentrations are highest at lower trophic levels and thus measurements throughout the food web—not only in the top trophic level—are needed. With respect to NPAHs, our two recent reports^{15,21} represent the only measurements in the Great Lakes.

Large anthropogenic emissions of PAHs in the Great Lakes region date back to at least the Industrial Revolution. The National Emissions Inventory quantified annual emissions at county, state, and national levels for 2002, 2005, 2008, and 2011,²⁷ and an earlier program of the Great Lakes Commission estimated emissions from 1993 to 2008.²⁸ These estimates are based on emission factors and the number and activity of point, area, and mobile sources. The development of accurate and comprehensive inventories is challenging: PAHs are emitted from numerous sources that are difficult to enumerate and

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characterize; emission factors are highly variable and uncertain; and measurements are expensive and scarce. Alternatively, emissions can be derived from the depositional record of PAHs present in sediments. Both current and historical emissions can be derived using PAH concentrations measured in surficial sediments and sediment cores using multimedia models in an inverse manner that accounts for transport and degradation processes. This approach accounts for all sources affecting the lake since sediments tend to be the ultimate sink for many contaminants. However, models must represent all source-to-sink processes accurately, and emissions of a compound that is completely transformed cannot be derived. Overall, however, comparisons between results obtained using emission factor and inverse modeling approaches is diagnostic and helpful in reconciling measurements and predictions which were based on emissions factors.

Fugacity-based models permit relatively simple yet effective multimedia analyses of chemical fate.²⁹ Such models have been used for persistent organic pollutants (POPs), including PAHs in Southern Ontario and Quebec, Canada.^{30,31} Level IV (dynamic) fugacity models also have been used for polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), brominated flame retardants,^{32–34} and polybrominated biphenyls (PBBs) in aquatic food webs.^{32,35}

This study investigates the appropriateness of fugacity models for predicting the fate of PAHs and NPAHs in Lake Michigan, and evaluates the use of inverse modeling to estimate emission rates. Steady-state (Level III) models are developed for PAHs and NPAHs for Lake Michigan, predicted PAH concentrations are compared to recent measurements in Lake Michigan sediment and fish, and NPAH emission rates are derived using inverse modeling. Level IV models are used to reconstruct PAH emission trends by matching historical records of PAH accumulation rates preserved in sediment cores. (NPAHs have not been measured in sediment cores.) Parameter uncertainty is evaluated using Monte Carlo (MC) analyses.

MATERIALS AND METHODS

Chemicals and Modeling Approach. We considered the 16 EPA priority PAHs³⁶ and the five NPAHs detected at relatively high concentrations in diesel exhaust, fish, and sediments^{15,21,37–39} (i.e., 1-nitronaphthalene, 2-nitronaphthalene, 2-nitrofluorene, 1-nitropyrene, and 6-nitrochrysene).

The Level III fugacity-based model is a steady-state (time invariant), nonequilibrium model with air, water, soil, and sediment compartments that is relatively simple and well suited for screening-level analyses. The model is detailed elsewhere,²⁹ and available from the Canadian Centre for Environmental Modeling and Chemistry (Level III version 2.80).⁴⁰ The mass balance equations are listed in the Supporting Information (SI) as eqs S1–S4. An equivalent model was developed in Excel (Microsoft Inc., Redmond, CA) to facilitate uncertainty analyses using @Risk software (Palisade Corporation, Ithaca, NY).

The dynamic (time varying) and nonequilibrium Level IV model included the same compartments described above, and mass balance equations are presented as SI eqs S6–S9. Transport parameters (D , mol/Pa-h)²⁹ were obtained from the Level III model results. Emissions and background concentration data use time-dependent functions (described later). Historical emission rates were derived for two PAHs: benzo[a]pyrene (B[a]P), a heavier (5-ring) compound

considered among the most toxic of PAHs and widely studied; and phenanthrene (PHE), a lighter (3-ring) compound found at relatively high concentrations in Lake Michigan sediments and fish.^{15,21}

The bioaccumulation model used eight species to represent Lake Michigan's food web coupled by a feeding matrix (described later). For each species, chemical uptake comes from water intake and food consumption, and elimination occurs through metabolism, egestion, discharge through gills, and organism growth (growth dilution). The steady-state and dynamic mass balance equations for each species are presented as SI eqs S5 and S10, respectively.

Model Inputs. Physiochemical and Food Web Parameters. The study area encompassed the Lake Michigan basin (SI Figure S1) and included air, water, soil, and sediment compartments. Environmental properties are presented in SI Table S1. Physiochemical properties of the chemicals and degradation half-lives (bulk parameters combining biotic and abiotic processes) were obtained from EPISuite⁴¹ and are listed in SI Section 1.3. The Lake Michigan food web included eight species: plankton, mysid, *Diporeia*, sculpin, rainbow smelt, bloater, alewife, and lake trout. Details of the food web are presented in SI Section 1.4.

Emissions and Background Concentrations. Of the total PAH loadings into Lake Michigan, atmospheric deposition (including wet and dry deposition, rain dissolution, and air–water diffusion) accounts for an estimated 80%, effluent discharges contribute 2–16%, and petroleum spills provide 10–15%.² We previously apportioned sources of PAHs in surficial sediments collected from Lake Michigan in 2011 to traffic (53%), coal power plants (25%), coal-tar pavement sealants (15%), and coke ovens (7%).¹⁵ Information regarding PAH loadings via runoff (water and sediment) or transfers via lake or river flows is unavailable. Runoff from coal-tar derived sealants applied to roads has been shown to be a significant source in other regions.^{42,43} For simplicity, PAH loadings included only emissions to air and discharges to water (including petroleum spills, effluent discharges, and urban runoff). Air emissions were assumed to comprise 90% of total loadings. The Level III model used annual PAH emission estimates reported in the 2008 Great Lakes Regional Air Toxic Emissions Inventory (SI Section 1.5).²⁸ Background concentrations for the Level III model (SI Table S6) were estimated using measurements near Lake Michigan and in other areas (SI Section 1.5).

NPAH Emissions. NPAHs arise primarily as products of incomplete combustion and from atmospheric transformation of PAHs.⁷ Thus, urban runoff and effluent discharge are anticipated to be small, and so only airborne NPAH emissions were considered. Year 2011 emission rates of NPAHs were estimated using our 2011 measurements of NPAH concentrations in surficial sediments collected at 24 sites across southern Lake Michigan and the Level III model used in an inverse manner. (Background concentrations were discussed above.)

Reconstruction of Historical PAH Emissions. Emission trends from 1850 to 2011 for B[a]P and PHE were reconstructed using two sources of sediment data. Sediment concentrations from 1850 to 1990 used a Lake Michigan sediment core study.¹⁷ Reported PAH accumulation rates (ng/cm²·yr) were divided by mass sedimentation rates (g/cm²·yr) to estimate sediment concentrations (ng/g dw, where dw = dry weight), and concentrations estimated for four sites located

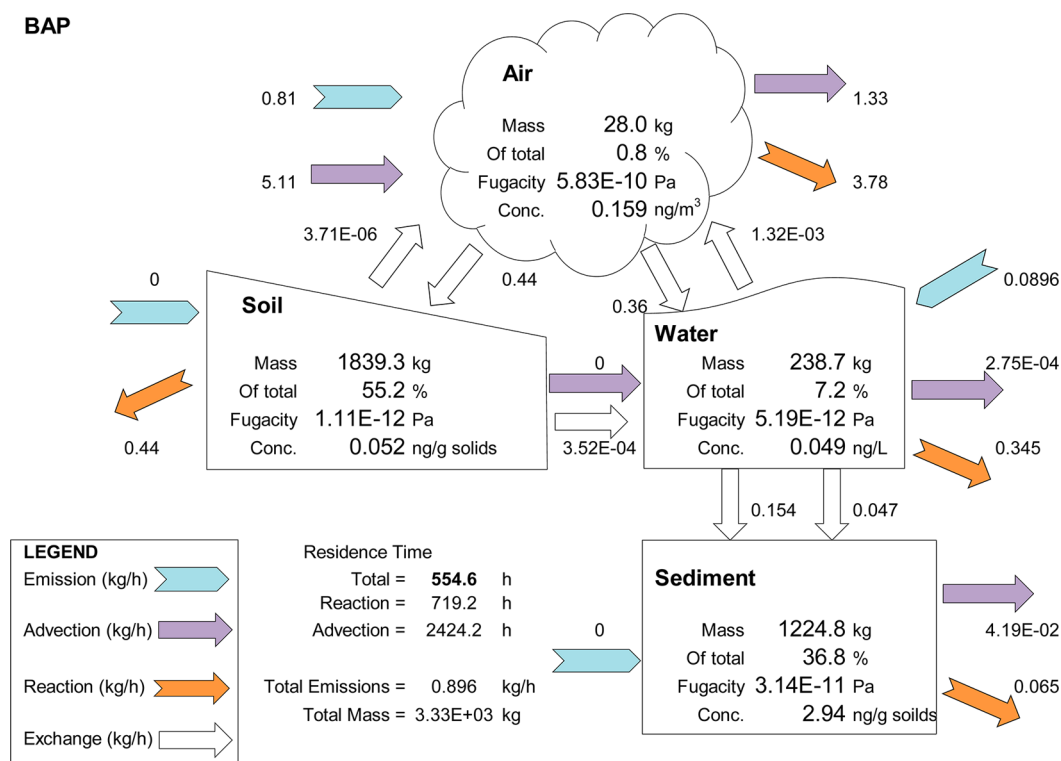


Figure 1. Level III mass balance diagram showing fluxes (kg/h) of benzo[a]pyrene in Lake Michigan. Adapted from ref 61. The size of the arrows is NOT proportional to the magnitude of the fluxes. The diagram for phenanthrene is shown in SI Figure S3.

along a north–south transect of Lake Michigan (18, 19, 47s, 68k) were averaged. (Site 70m was excluded due to mixing issues.) For 2011, we averaged the surficial sediment concentration measured at 24 sites across southern Lake Michigan in 2011.¹⁵ Concentrations between 1990 to 2011 were interpolated from these two studies. The fugacity in sediment (f_4 , Pa) was calculated as $f_4 = C_{\text{sed}} \cdot \rho_{\text{sse}} / (Z_{\text{sse}} \cdot \text{MW} \cdot 10^6)$, where C_{sed} = concentration in sediment (ng/g dry), ρ_{sse} = density of sediment solids (kg/m³), Z_{sse} = fugacity capacity in sediment solids (mol/m³·Pa), and MW = molecular weight (g/mol).

The Level IV (dynamic) model was used to estimate B[a]P emissions trends from 1850 to 2011. Again, 90% of the total loadings were attributable to air (E_1) and 10% to water (E_2). Background concentrations in air were assumed to follow the same trend as air emissions, and background concentrations in water were assumed to be zero (the same assumption used in the Level III models). For B[a]P and PHE, the background concentration in air (C_{b1} , ng/m³) was assumed to be $0.75 \times E_1$ and $3 \times E_1$, respectively, based on 2008 measurements (B[a]P: $E_1 = 0.81$ kg/h, $C_{b1} = 0.61$ ng/m³; PHE: $E_1 = 9.9$ kg/h, $C_{b1} = 30.2$ ng/m³). The time trend of E_1 was assumed to be a polynomial function with several unknown parameters. These parameters and f_4 were estimated by solving the set of ordinary differential equations (ODEs; SI eqs S6–S9) representing the Level IV model, and minimizing the sum of the squared differences between predicted and measured f_4 across all time points using the available sediment data (shown later in Figure 2). These calculations used Matlab R2013b (MathWorks Inc., Natick, MA), the stiff solver ode23tb for the ODEs, and function *fminsearch* (Nelder–Mead simplex direct search).

Uncertainty Analysis. The modeling involved many possible sources of uncertainty. A sensitivity analysis using

nominal model parameters for B[a]P indicated that the background concentration in air, air residence time, vapor pressure, log K_{ow} , emission rate, and degradation half-life (in fish) were the most influential input parameters. Large uncertainties are associated with several of these parameters. As examples, most half-lives were EPISuite estimates (not experimental results) for which uncertainties may exceed a factor of 10;^{32,44} inventory emission rates may be incomplete or possibly overstated (the 2002 B[a]P emission estimates were revised downward by 32%⁴⁵ and emission rates for Lake Michigan were scaled back from those reported for the entire Great Lakes basin); background concentrations of PAHs were available only through 2003; and background NPAH levels were based on measurements taken elsewhere (SI Section 1.5).

Parameter uncertainty was addressed using MC analysis. For the Level III PAH model, a uniform distribution was used for each degradation half-life with lower and upper bounds of 1/10 and 10 times the EPISuite estimate, respectively. For emission rates and background concentrations, log-normal distributions were used with confidence factors (CF) of 3 and 2, respectively. (CF = 3, for example, means that 95% of the trial values will lie between one-third and three times the median.) NPAH modeling of emission rates used the same uncertainties for degradation half-lives. Background estimates used a CF of 5 and a log-normal distribution, reflecting greater uncertainty.

For each modeled compound and each application, the MC analysis used 1000 simulations, and confidence intervals were expressed using the 5th and 95th percentiles of the model outputs. MC analyses were conducted using @Risk 6.1 (Palisade Corporation, Ithaca, NY) and Excel (Microsoft Inc., Redmond, WA).

Table 1. Concentrations, Parameters, and Transfer Rates for B[a]P in the Lake Michigan Food Web

	plankton	mysid	<i>Diporeia</i>	slimy sculpin	rainbow smelt	bloater	alewife	lake trout
fugacity (Pa)	5.27×10^{-12}	5.66×10^{-12}	2.76×10^{-11}	7.72×10^{-13}	4.58×10^{-13}	4.61×10^{-13}	4.70×10^{-13}	1.72×10^{-14}
concentration (pg/g wet)	453	1295	4738	354	105	264	188	14.8
equilibrium BCF	2.49×10^4	6.64×10^4	4.98×10^4	1.33×10^5	6.64×10^4	1.66×10^5	1.16×10^5	2.49×10^5
BAF (g/L)	9.2	26	97	7.2	2.1	5.4	3.8	0.30
transfer rates ($\times 10^{-16}$ mol/h)								
uptake by respiration in water	0.45	11	0	118	227	512	344	5207
uptake by respiration in sediment	0	0	6.0	0	0	0	0	0
uptake from food	0	12	0	734	533	6622	2309	50673
loss by respiration	0.44	11	5.3	17	19	44	30	17
loss by egestion	0	1.8	0	13	18	65	35	175
loss by metabolism	0.001	5.5	0.40	807	709	6917	2548	55543
loss (dilution) by growth	0.009	4.3	0.31	16	14	108	40	145

RESULTS AND DISCUSSION

Level III Model. Multimedia Model for PAHs. B[a]P transfers and reservoirs predicted by the Level III model in the modeled domain are depicted in Figure 1 (based on parameters in SI Tables S1, S2 and S6). The total atmospheric input, 5.9 kg/h, was dominated by advective flows (86% of the total), while local emissions made up the balance (14%). Airborne B[a]P was lost by advection (22%) and reaction (64%), and relatively little was deposited into the lake (6%) and surrounding land (7%). The airborne concentration over the lake, 0.16 ng/m³, agrees with mean levels reported in 1994–95 (~0.2 ng/m³)¹² The lower prediction may reflect emission decreases in the past decade or two. (Newer measurements are not available.)

In water, the major inputs were atmospheric deposition (80%) and direct discharges to water (20%). Losses were dominated by reaction and deposition to sediments. Advective losses were negligible given the Lake's long hydrologic retention time (99 years). Of the 0.45 kg/h B[a]P entering the lake, reactions in the water column consumed 76%, net transfers to sediment represented 24%, and evaporation was negligible. The B[a]P concentration predicted in water (0.05 ng/L) was eight times lower than mean of samples collected near Chicago in 1994–1995 (0.4 ng/L),²⁰ however, these measurements likely were affected by near-shore sources and thus do not represent the lake-wide average predicted by the model. (Additional reasons for discrepancies are discussed later.) The B[a]P concentration predicted in sediment (2.9 ng/g dw) matched our 2011 measurements (mean of 2.7 ng/g dw; range of 1.0–10.2 ng/g dw). The principal loss mechanisms for the sediment were reaction (61%) and burial (39%).

Predictions of all 16 PAHs are summarized and compared to measurements in air, water, soil, and sediment in SI Table S7. Results of MC analyses, which show the range of concentrations in sediments attributable to uncertainty in degradation rates, emission rates, and background air concentrations, are shown in SI Figure S4. For PAHs with three or fewer rings, most of the PAH mass was found in the water column and the atmosphere, while the dominant reservoirs for PAHs with four or more rings were soils and sediments. Modeled airborne concentrations closely matched measurements,¹² and reflected the dominance of advective flows and rapid atmospheric

reactions. Predictions in water and sediments had greater variation, and measurements generally exceeded point predictions, although measurements of most PAHs fell into the 5th to 95th percentile range estimated by the MC analyses (SI Figure S4). (Predicted abundances of most compounds also agreed with observations, with the exceptions of B[a]P and BghiP, although BghiP concentrations matched measurements.) The MC analyses, which used very wide uncertainty ranges (10-fold range for degradation half-lives, 3-fold for emission rates, and 2-fold for background concentrations), tended to under-predict concentrations of most PAHs in sediments, although B[a]P was overpredicted. Uncertainties for B[a]P used in the MC analysis appear excessive. This compound is widely studied, and parameters for B[a]P have lower uncertainties, thus it is unsurprising that the deterministic model gave a close match. However, uncertainties for other PAHs (as well as NPAHs) are large. The MC analyses are helpful in indicating the approximate and possible ranges of predictions.

Several factors can explain the apparently low predictions of PAH concentrations in water and sediment. First, as noted, water sampling sites were close to Chicago and sediment samples were collected in southern Lake Michigan; both sets of measurements may be dominated by local sources and not reflect the lake-wide averages given by the model. Second, EPISuite generally overestimates the reactivities of persistent organic pollutants⁴⁴ (e.g., estimated half-lives in water, soil, and sediments for PCBs were 1–2 orders of magnitude lower than those in other references).⁴⁴ If values for PAH parameters were similarly biased, then PAH concentrations will be underestimated. Third, given the lack of data for effluent discharge and petroleum spills, emissions into water may be underestimated. Similarly, the zero background concentration in water inflows assumed will contribute to the underestimate. Finally, the Level III model assumes steady-state and does not account for (higher) emissions in earlier years. However, measured concentrations in sediments may reflect earlier periods with higher emission rates (e.g., as shown by declining trend of airborne PAH concentrations).¹⁴ All of these factors might explain the low concentrations in sediments predicted using the 2008 emission rates.

Table 2. NPAH Emission Rates and Environmental Concentrations Derived Using the Level III Model and Concentrations Measured in Sediment

compound	measurements ^a	model predictions ^b			
	sediment (ng/g dry)	air (ng/m ³)	water (ng/L)	soil (ng/g dry)	emission to air (kg/h)
1-nitronaphthalene	0.61 (0.39)	8.6 (6.3–41.2)	11.7 (11.6–14.2)	0.12 (0.02–0.55)	69 (11–444)
2-nitronaphthalene	0.52 (0.42)	4.7 (3.2–25.7)	8.5 (8.3–10.4)	0.10 (0.01–0.51)	31 (0–304)
2-nitrofluorene	0.83 (0.55)	4.5 (2.9–25.9)	8.7 (8.6–11.2)	0.15 (0.02–0.89)	46 (25–298)
1-nitropyrene	2.67 (1.41)	0.09 (0.06–0.45)	0.17 (0.17–0.23)	0.16 (0.02–0.81)	0.3 (0–4.3)
6-nitrochrysene	3.22 (1.67)	0.04 (0.03–0.16)	0.11 (0.11–0.15)	0.29 (0.03–1.24)	0.2 (0–2.0)

^aMean concentrations across 24 sampling sites in southern Lake Michigan (standard deviation in parentheses). ^bData presented are median (5th percentile–95th percentile).

Each model compartment was assumed to be homogeneous and time-invariant, thus, seasonal effects (e.g., temperature changes affecting partitioning and degradation rates) and site-to-site differences (e.g., local differences in degradation rates and sources) were not represented. Ideally, model predictions would incorporate variation as well as uncertainty. While depending strongly on input parameters, the MC simulations illustrate the possible or likely ranges of concentrations.

Bioaccumulation of PAHs. Predicted water and sediment concentrations of PAHs (SI Table S7) were used in the food web model to demonstrate overall model performance using estimated emission rates and physiochemical parameters without corrections or calibrations using water, sediment, or other measurements. Detailed food web model results for B[a]P, presented in Table 1, show that bioaccumulation factors (BAF = concentration in the organism divided by the concentration in water) generally decreased at higher trophic levels. For example, the highest concentration was predicted in *Diporeia* (4738 pg/g ww), which resides in sediments where B[a]P concentrations are relatively high. Further, *Diporeia* is unable to efficiently metabolize B[a]P.^{46,47} Slimy sculpins (354 pg/g ww) had the highest concentrations among prey fish; its diet consists largely of *Diporeia*. In contrast, lake trout efficiently metabolizes PAHs and had the lowest level (15 pg/g ww), which agreed closely with recent (2011–2012) measurements in Lake Michigan lake trout (average: 18.4 pg/g; range: 5.6–43.4 pg/g).²¹ Throughout the food web, B[a]P uptake was dominated by food consumption (except for plankton and *Diporeia* which do not consume other organisms), in large part due to the lipophilicity of B[a]P. This PAH was lost primarily through respiration in invertebrates (plankton, mysid, *Diporeia*) and through metabolism in fish.

The food web model results are summarized in SI Table S8. For PAHs with 5 or more rings (BBF to BghiP), predicted and observed concentrations in lake trout are within a factor of 5 with the exception of BghiP (predicted/observed ratio ≈ 0.04): EPISuite gave an especially short metabolic half-life in fish (7 h) for this compound, and BghiP concentrations predicted in water and sediments (and used in the food web model) were lower than observations (SI Table S7). For PAHs with 4 or fewer rings, concentrations in lake trout were generally overpredicted. This discrepancy, which would have been larger had measured water and sediment PAH concentrations been used in the food web model, can result from multiple reasons. For example, underestimates of clearance rates in aquatic organisms (e.g., a half-life of 17 h has been reported for anthracene in bluegill sunfish⁴⁸ compared to the 61 h estimated by EPISuite); erroneous assumptions regarding half-lives (necessary given the lack of information for fish and aquatic

invertebrates); and gut absorption efficiencies (from water and food) that differ among compounds for a particular species (identical efficiencies were assumed). For PAHs with ≥ 5 rings and higher log K_{ow} , predicted concentrations in water were low, and the assumed absorption efficiencies gave concentration predictions in fish that were within a factor of 5 of observations. However, for the 2–4 ring PAHs (especially NAP, PHE, and FLA), predicted concentrations in water and thus fish were high compared to available data (SI Table S8). Modeling used the same gut absorption efficiency for all PAHs, which is relatively constant for organic compounds with log K_{ow} from 5 to 7.⁴⁹ However, we suspect efficiencies are lower for less lipophilic compounds. Additional data regarding PAH uptake and metabolism in biota are needed to refine predictions and evaluate sources of discrepancies.

The Lake Michigan food web has changed considerably in recent years. The native amphipod *Diporeia*, once the dominant benthic organism in Lake Michigan and an important prey species for many forage fish, has been rapidly declining since the 1990s following the invasion of zebra and quagga mussels.^{50,51} Its average population density in Lake Michigan has dropped from 4000/m² in 1997 to 57–1409/m² in 2009.⁵² Diets of a few fish (e.g., lake whitefish) have shifted to include zebra and quagga mussels;⁵⁰ diets of other species (alewife, bloater, smelt, and sculpin) still consist of mainly *Diporeia* (although declining in ration), mysid, and plankton.⁵³ The mussel population, which can cover a large fraction of the sediment surface, may play important roles in contaminant cycling. For example, zebra mussels both bioconcentrate PAHs from the water column, thus reducing PAHs that reach sediments, and deposit contaminated feces and pseudofeces, thus increasing PAH concentrations in sediments.⁵⁴ In addition, Lake Michigan has become more oligotrophic due to reduced phosphorus loadings,⁵⁵ decline of energy-rich *Diporeia*, and the increase of energy-poor zebra/quagga mussels,⁵⁰ with possible impacts of reducing the organic carbon in surficial sediments that might then increase PAH bioavailability. The counterbalancing effects attributed to zebra and quagga mussels, as well as those associated with other species in the food web, could be addressed in future modeling and monitoring efforts.

NPAH Emissions. NPAH emissions to the Lake Michigan airshed were derived using inverse modeling, parameters derived mainly from EPISuite⁴¹ and our 2011 NPAH measurements in Lake Michigan sediments,¹⁵ and MC analyses to represent parameter uncertainty associated with degradation half-lives and background airborne concentrations. Emissions included both airborne releases (e.g., from combustion sources) and secondary formation (e.g., from atmospheric reactions).

Of the five NAPHs considered, 1-nitronaphthalene had the highest emission rate (median of 69 kg/h), considerably above

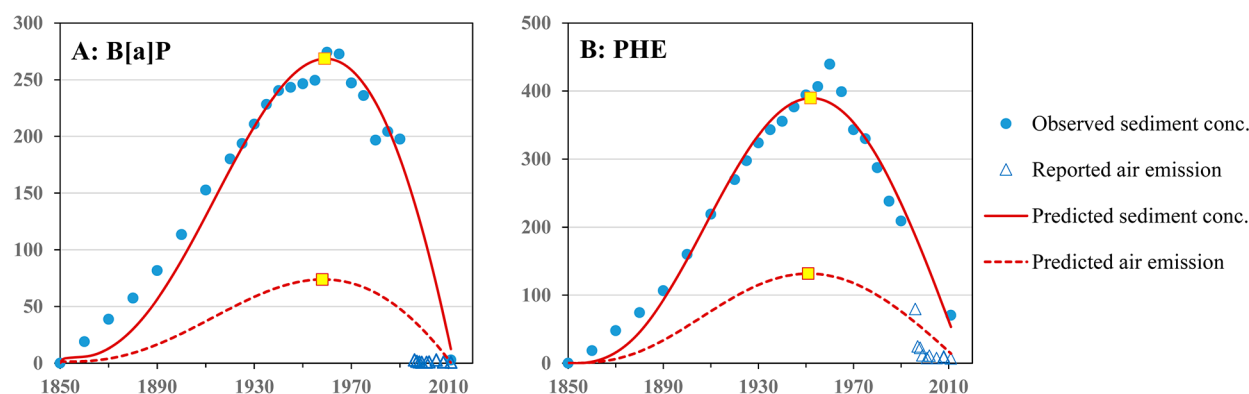


Figure 2. Air emission rates (kg/h) and sediment concentrations (ng/g dw) of (A) B[a]P and (B) PHE. Yellow squares indicate the peaks.

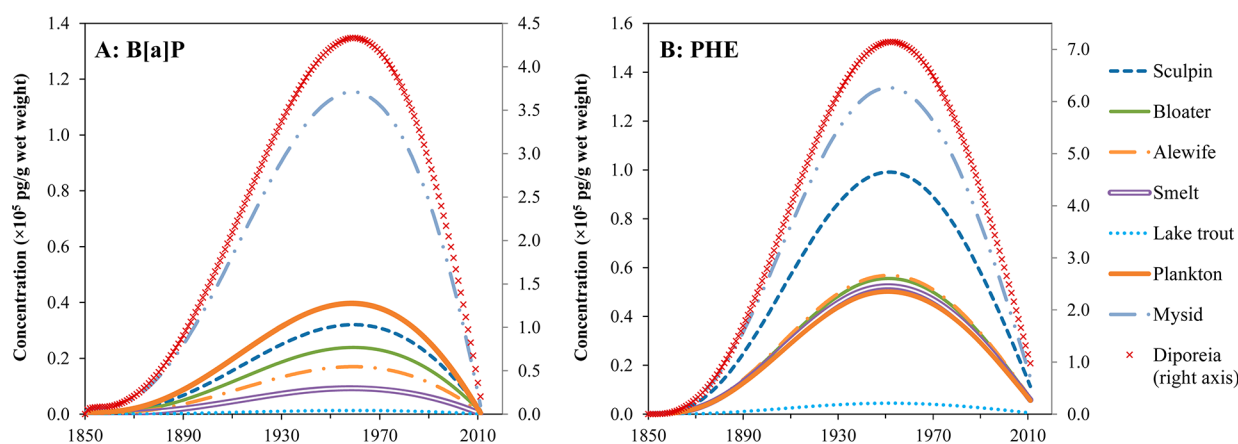


Figure 3. Predicted trends of (A) B[a]P and (B) PHE concentrations in eight species in the Lake Michigan food web. *Diporeia* is plotted on the right axis, while other species are plotted on the left axis.

the others, including those found at much higher concentrations in sediments (e.g., 1-nitropyrene, 6-nitrochrysene) (Table 2). This results from physiochemical properties: for example, compounds with fewer rings tend to partition into air and water, and usually degrade much faster than compounds with more rings (SI Table S2). Estimated median emission rates were lower than emission rates of parent PAHs, except for 2-nitrofluorene (46 compared to 2.4 kg/h of fluorene), which suggests large primary emissions of 2-nitrofluorene from diesel engines or other sources.^{38,39,56} The emission estimates depend on a number of estimated parameters, for which uncertainties are high, and NPAH measurements in air, water, and soil are needed to confirm these results.

Dynamic Modeling. Historical PAH Emissions. The Level III models assume steady-state conditions and do not account for changes in historical emissions. Significant anthropogenic PAH emissions began in the 19th century, but emission inventories are available only since 1993.²⁸ Here, a dynamic (Level IV) model, which requires continuous emission data, is used to model PAHs in Lake Michigan, and PAH records in sediment cores and inverse modeling are used to reconstruct historical emission profiles. For B[a]P, sediment concentrations predicted by the Level III model agreed well with measurements (SI Table S7), thus the Level IV model used the same degradation half-lives. For PHE, the Level III model underestimated sediment concentrations (SI Table S7), probably because degradation half-lives were underestimated, as discussed earlier. To improve model fit, degradation half-lives

for PHE in soil and sediment provided by Mackay et al.³⁰ were used (SI Table S9) instead of the EPISuite estimates.

Estimated airborne emission rates of the two PAHs and the concentrations predicted in sediments (using these emissions) are shown in Figure 2, along with the levels measured in sediment cores. Following trends in the sediment concentrations, emissions gradually increased from 1850 until the 1950s. This has been attributed to increased industrialization and coal use;^{17,57} other important sources may include vehicle emissions, biomass burning (including forest fires), and secondary emissions. Emissions sharply declined in the early 1970s, and current (2011) emission rates have returned to 1850–1880 levels, potentially due to a transition to cleaner fuels (coal to oil and natural gas), reduced coke production, changes in coking technology, and emission controls on industry and vehicles.^{17,19,57,58} Predicted and observed sediment concentrations matched closely ($R^2 > 0.95$). B[a]P and PHE trends were very similar; for example, both peaked in the 1950s. The PHE peak occurred a few years earlier than the B[a]P peak, but this may be due to variation in the data or the fitting approach used. In sediments, concentrations lagged emission rates by one year, representing the time PAHs emitted to air need to reach lake sediments. In comparison, a longer (four year) lag was found in modeling hexabrominated biphenyl in Lake Huron,³² possibly due to differences in degradation half-lives, inventory errors, or other reasons.

The derived emission rates exceed those compiled in the Great Lakes Regional Air Toxic Emissions Inventory (GLRATI) for B[a]P by 10–20 times and for PHE by 2–3

times (Figure 2). Uncertainties in PAH and other toxics inventories can be very large and are rarely quantified. In 1997, the GLRATI reported that (on- and nonroad) mobile sources contributed 27% of PAH emissions, while receptor-model derived apportionments (using Lake Michigan sediments) estimated 45%.⁶⁰ The GLRATI also indicated that emissions of B[a]P were unchanged from 1996 to 2008, while PHE emissions declined 8-fold. In an application in the Athabasca (Canada) oil sands region, inverse modeling also showed large discrepancies in PAH emissions (100- to 1000-fold higher than estimates in the National Pollutant Release Inventory).⁵⁹

Although not surprising that inventory estimates based on emission and activity factors diverge from estimates using receptor or inverse modeling, the large discrepancies highlight the need to reconcile emission estimates. With appropriate monitoring data, receptor- or inverse modeling-based emission estimates may increase the reliability of estimates and account for all emission sources, especially since sediment tends to be the ultimate sink for PAHs. Whereas the model estimates complement existing inventories and can point out possible deficiencies, additional measurements are needed to confirm that the environmental measurements are representative and temporally complete, especially the period between 1990 and 2011 that was interpolated due to data gaps, and more accurate estimates of model parameters are needed to reduce uncertainties.

PAH Bioaccumulation Trends. Food web concentrations calculated using the dynamic food web model and derived B[a]P and PHE emission rates are shown in Figure 3. For B[a]P, the same metabolic rates (for the eight species) in the steady-state model were used. For PHE, all half-lives were reduced 6-fold (SI Table S9) to account for the overprediction seen in the steady-state predictions for lake trout (SI Table S8). With these parameters, predicted B[a]P and PHE concentrations in lake trout for year 2011 were 56 and 524 pg/g, respectively, which closely matched our measurements (6–43 and 17–850 pg/g, respectively).

B[a]P and PHE concentration trends predicted in aquatic invertebrates and fish followed trends derived for emission rates and sediment concentrations. B[a]P concentrations in plankton peaked in 1958, corresponding to the highest concentration in water. In contrast, concentrations in other species show a one year lag, shorter than the more bioaccumulative chemicals discussed earlier. PHE concentrations in plankton, mysid, and smelt (and water) peaked in 1951; concentrations in other species peaked in 1952. Otherwise, concentration trends through the food web were similar to those predicted by the steady-state model (e.g., B[a]P concentrations were highest in *Diporeia*, followed by mysid, plankton, prey fish, and lake trout). PHE trends were similar, except that concentrations in sculpins exceeded those in plankton due to sculpin's efficient biotransformation (metabolism) of B[a]P. PHE concentrations in other prey fish were similar, reflecting the significance of uptake from water.

Significance and Application. The behavior of PAHs and NPAHs in Lake Michigan and the aquatic food web is complex, and multimedia models are essential for integrating the multiple governing factors (e.g., emission rates, background concentrations, reaction/metabolic half-lives, gut absorption efficiencies, and transfer coefficients). This study demonstrated that the distribution of many PAHs can be predicted across multiple compartments, and inverse modeling was used to reconstruct historical trends of PAHs and provide the first estimates of

NPAH emission rates in the basin. The use of models for estimating emission rates from environmental measurements is practical, diagnostic, and useful for improving emission inventories. However, for PAHs with ≤ 4 rings, more accurate parameters are desirable, especially for biota uptake and metabolic rates, and additional measurements are needed to evaluate model predictions.

■ ASSOCIATED CONTENT

Supporting Information

Detailed description of modeling methods and parameter values, additional tables and figures presenting detailed results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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