Integrated ecological and chemical food web accumulation modeling explains PAH temporal trends during regime shifts in a shallow lake

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\textbf{Abstract}

Shallow lakes can switch suddenly from a turbid situation with high concentrations of phytoplankton and other suspended solids to a vegetated state with clear water, and vice versa. These alternative stable states may have a substantial impact on the fate of hydrophobic organic compounds (HOCs). Models that are fit to simulate impacts from these complex interactions are scarce. We developed a contaminant fate model which is linked to an ecosystem model (PCLake) for shallow lakes. This integrated model was successful in simulating long-term dynamics (1953-2012) of representative polycyclic aromatic hydrocarbons (PAHs) in the main biotic and abiotic components in a large shallow lake (Chaohu in China), which has undergone regime shifts in this period. Historical records from sediment cores were used to evaluate the model. The model revealed that regime shifts in shallow lakes had a strong impact on the fate of less hydrophobic compounds due to the large storage capacity of macrophytes, which accumulated up to 55.6% of phenanthrene in the clear state. The abrupt disappearance of macrophytes after the regime shift resulted in a sudden change in phenanthrene distribution, as the sediment became the major sink. For more hydrophobic compounds such as benzo(a)pyrene, the modeled impact of the regime shift was negligible for the whole environment, yet large for biotic compartments. This study is the first to provide a full mechanistic analysis of the impact of regime shifts on the fate of PAHs in a real lake ecosystem.

\section{1. Introduction}

Freshwater shallow lake ecosystems often suffer from water quality deterioration due to eutrophication (Conley et al., 2009). The response of these systems to eutrophication is non-linear, reinforced by multiple feedback mechanisms (Carpenter et al., 1999) that lead to alternative stable ecosystem states, i.e. a clear, macrophyte-dominated state, and a turbid, phytoplankton-dominated state (Scheffer et al., 2001). Such systems are stable in either of the states (Scheffer et al., 1993) but can shift from one state to another surprisingly, when a threshold of a certain external condition is crossed (e.g. nutrient loading), which is generally referred to as a ‘regime shift’ (Scheffer and Jeppesen, 2007). Over the last decades, many shallow lakes around the globe have undergone such a regime shift from clear to turbid state mainly due to severe pressure from anthropogenic activities (Kong et al., 2017; Wang et al., 2012).

Meanwhile, freshwater lake ecosystems in highly populated areas are increasingly contaminated with hazardous chemicals such as hydrophobic organic contaminants (HOCs) (Schwarzenbach et al., 2006). These HOCs are distributed among various compartments in the lake environment and accumulate in the aquatic food web, thereby threatening ecological functions due to toxicity to organisms (Qin et al., 2013b), and potentially undermining human health if contaminated aquatic products are consumed (Wu et al., 2017).
2. Materials and methods

2.1. Study area

Lake Chaohu (31°25′28″–31°43′28″N, 117°16′54″–117°51′46″E) is the fifth largest freshwater shallow lake in China with a surface area of 760 km² and an average depth of 3 m, located in the most developed region among the lower reaches of the Yangtze River floodplain (Fig. 1). The lake used to provide important ecological services to the catchment area, e.g., drinking water supply for large cities Hefei and Chaohu. However, the lake ecosystem has undergone regime shifts between clear and turbid states since the 1950s (Kong et al., 2017). The heavy flood occurring in 1954 induced a regime shift into a turbid state in this lake, which shifted back to a clear state before 1960 (Kong et al., 2017). The onset of the sluice in 1963 (Fig. 1), however, tipped the lake into a turbid state again, and increasing nutrient loadings (Kong et al., 2015) triggered the nuisance of phytoplankton blooms since 1980, which has lasted until now. The lake is no longer serving as the drinking water source to adjacent cities. Great effort has been invested into ecological restoration and management of this lake with however limited improvement in lake water quality and ecological status at the current stage (Kong et al., 2017). Meanwhile, the lake has been subjected to severe PAHs pollution (as well as black carbon) due to increasing energy consumption by biomass fuel combustion for heating in rural areas, vehicle emissions in urban areas and coal combustion at nearby power plants in the catchment (Qin et al., 2014). Reduction in PAHs input to the lake in recent years is not likely to happen due to intensified human activities in the lake catchment (Giesy et al., 2016).

2.2. Data collection

Phenanthrene (Phe), pyrene (Pyr) and benzo(a)pyrene (BaP), were selected to represent low-, moderate- and high-molecular-weight PAHs. Monthly concentrations of these PAHs were available for gaseous, aerosol particles and for suspended solids from May 2010 to April 2011, and aqueous phase from May 2010 to April 2012 (Qin et al., 2013a, 2014), at multiple sampling sites (Fig. 1). Other field data included PAHs in multiple groups of biota for human consumption in 2009 (Qin et al., 2013c) and in phytoplankton in 2012 (provided as Supporting Information). We further collected data from literature, including PAHs in surface sediment in 2011 (Li et al., 2014) and in soil close to the study site in 2007 (Wang et al., 2010). Additionally, we used PAHs concentrations in vegetation for Lake Taihu in 2014 (Tao et al., 2015) as a proxy for those in Lake Chaohu. This is based on the fact that: 1) both lakes are located in the lower Yangtze River floodplain, where the ecosystems are subjected to very similar (intense) human disruptions and pollution (Dearing et al., 2012); 2) Both lakes are large shallow lakes with similar eutrophication status since the 1980s (Janssen et al., 2014; Kong et al., 2017); 3) Both lakes are located in the area with similar intensity of PAHs emission (Zhang et al., 2007). Overall, PAH observations were available for model evaluation in all modeled compartments except for zooplankton. For all organisms, data on lipid fractions were available from our previous measurements (Qin et al., 2013c). In addition, PAH profiles were measured in the first 30 cm of two sediment cores (Fig. 1), which were collected with a Kajak gravity corer from the centers of the west and the east part of Lake Chaohu on August 23rd, 2011 (details for PAHs measurement provided as Supporting Information). The time series of historical PAHs records were used for the evaluation of the long-term model simulation. Chronologies were obtained by measuring 210Pb and 137Cs radionuclide activities in contiguous samples in the cores (details provided as Supporting Information). More details...
regarding analytical procedures for $^{210}$Pb and $^{137}$Cs radionuclide activities in the sediment were reported before (Kong et al., 2017).

2.3. Model development

The model framework is composed of an ecological module (PCLake model) and a contaminant fate model that includes an abiotic module and a biotic (foodweb) module (Fig. 2). Model equations are provided as Supporting Information. Important environmental processes (e.g. water-sediment interaction) and dynamics of the food web components in Lake Chaohu are simulated using PCLake (Fig. 2). PCLake is a well-developed ecosystem model for shallow lakes in the context of the alternative stable states theory (Janse, 2005). This model has been adapted for Lake Chaohu in our previous study and fitted to field observations (including nutrient levels, water quality indicators and biomass of various biota components) in both short-term (2008-2013) and long-term (1953-2012) simulations (Kong et al., 2017). PCLake has a food web module that is similar to the biotic module in the contaminant fate model in the present study. Therefore, the biomass for different organism groups as simulated by PCLake (Fig. S1) is used as input for the simulations of the food web PAH bioaccumulation model. This is based on the assumption that PAH toxicity had no influence on the biomass and abundance of species, which is reasonable for the present case study because the PAH concentrations (total and individual PAH) in both sediment cores were generally lower than the threshold effect concentration (TEC), and were always below the probable effect concentration (PEC) (MacDonald et al., 2000) (Fig. S2).

For the contaminant fate model, the abiotic module is a fugacity-based level IV fate model for lakes based on previous studies (Kong et al., 2014; Xu et al., 2013), with an additional soil compartment in the lake basin. The water compartment is assumed well-mixed in the lake basin. The water compartment is assumed well-mixed in the lake basin. The sediment compartment (i.e. detritus) serves as an additional group in the food web. Modeled processes include exchange through gills from water or pore water in sediment ($D_W$), uptake from food ($D_F$), loss by fecal egestion ($D_E$), dilution ($D_D$), loss by metabolism ($D_M$) and loss by predation ($D_P$). For the three fish groups, we added the process of production ($D_P$) representing the influence of fishery. The exchange with water for fish groups is modeled following Arnot and Gobas (2004), which is also applied for invertebrates (zooplankton and zoobenthos).

Growth dilution and metabolism for both fish and invertebrates are modeled as first-order kinetic processes, while the PAH metabolic transformation rates are approximated following Moermond et al. (2007). Note that metabolism is found to dominate PAH elimination from fish and invertebrates and is thus important for the trophic transfer of PAHs in aquatic ecosystems (Wan et al., 2007). For modeling PAHs in macrophytes and phytoplankton, we used similar principles as those for fish and invertebrates, with modifications based on the uptake model for phytoplankton from Dachs et al. (1999) (SI text). Bioaccumulation is modeled based on the foodweb interactions (Arnot and Gobas, 2004) and the dietary composition defined in Table S3. Finally, we modeled elimination by egestion as a constant fraction of the uptake from food, quantified as the limiting biomagnification factor ($Q$) (Campfens and Mackay, 1997).

2.4. Parameter determination

Definition, statistical data and sources for all the parameters in the contaminant fate model are listed in Tables S4-S6. There are 159 parameters in the model, including 46 environmental parameters, 21 chemical-specific parameters (mass transfer and physicochemical parameters) and 92 food web-related parameters. Twenty-one
parameters vary seasonally, whereas the other parameters remain constant throughout the simulation. The parameters were obtained from the relevant literature or calculated based on the conditions in Lake Chaohu (Tables S4–S6). Temperature corrections were applied to both subcooled liquid vapor pressure ($P_{25}$; Pa) and Henry’s law constant ($H_25$; Pa m$^3$/mol) at 25 °C (Lun et al., 1998; Paasivirta et al., 1999). Note that vapor pressure for the solid substance of the chemical, which is generally lower than that for the subcooled liquid of the chemical, can lead to an overestimation of the fugacity capacity of aerosol particles and thus to inaccurate predictions (Paasivirta et al., 1999). Sorption of PAH to black carbon (BC) in sediment was taken into account. Following previous approaches (Hauck et al., 2007; Koelmans et al., 2009), a whole-lake median literature value for the fraction of BC in sediment was applied ($f_{BC} = 0.002$). Other parameters for strong sorption of PAHs to carbonaceous materials and for metabolic transformation were based on Moermond et al. (2007). We used the bioconcentration factors for phytoplankton’s matrix and surface (BCFM and BCFs, respectively; m$^3$/kg) reported by Del Vento and Dachs (2002), adjusted by the factors $k_d$($k_d + k_c$) and $k_{des}$($k_{des} + k_c$), respectively, to account for the dilution effect of growth (Koelmans, 2014; Koelmans et al., 1995). The parameters $k_d$ (1/h), $k_{des}$ (1/h) and $k_c$ (1/h) are the depuration rate, the desorption rate of surface, and the growth rate of phytoplankton, respectively. Uncertainty exists when these parameters are extrapolated to other phytoplankton species (Del Vento and Dachs, 2002). However, as the experimentally determined values were not available for species in Lake Chaohu, we used literature data (Del Vento and Dachs, 2002). We assumed that species-dependent kinetic factors play a secondary role in determining the fate of POPs in aquatic environments, which has been proved valid for modeling other HOCs (Dachs et al., 1999).

To evaluate the robustness of the model and the ability of the model to predict the seasonality of PAH concentrations in Lake Chaohu, the long-term simulation was designed to investigate the impact of the catastrophic regime shift on the fate and dynamics of PAHs in the catchment of Lake Chaohu. Note that our model is 0-dimensional, which suffices for the present study because the lake is assumed to be well-mixed both horizontally and vertically. The external conditions were derived from our previous study (Kong et al., 2017), including water inflow and outflow, water depth, wind speed, water temperature and precipitation. Other boundary conditions such as emission inventories are provided as Supporting Information. For the short-term, initial values were the observations from March 2010 for concentrations in air and water, complemented with the available field observations for the other compartments. For the long-term, however, no data were available before the starting date. We assumed initial values to be two orders of magnitude lower than the average values for 2008–2013 based on the concentrations measured in the deepest (oldest) layers from sediment cores (Fig. S2). The model was implemented in Matlab (MathWorks, 2002). The differential equations were solved using a fourth-order Runge-Kutta method as available in Matlab (ode45), with a simulation time step of 1 h.

3. Results and discussion

3.1. Model evaluation in the short-term simulation

In the short-term simulation, our yearly (2-year for dissolved phase in water) average results fit well to the measured data for all modeled compartments (Fig. 3); two-thirds of the outcomes with a deviation smaller than a factor of 3, one-sixths with a deviation between a factor 3 and 5, and one sixths with a deviation between a factor 5 and 10. An acceptable deviation between measured and modeled values for contaminant fate models is 0.7 logarithm units or lower, i.e. a factor smaller than 5 (Cowan et al., 1995). Thus, five-sixths of the modeling results fall in the acceptable range. We found that model performance for suspended solids, phytoplankton and macrophytes are relatively less robust (with larger deviation), particularly for Phe and BaP. Moreover, previous studies showed that the underestimation of sorption of PAHs to sediment can be due to the neglect of strong nonlinear sorption to condensed carbonaceous materials such as BC in the sediment (Moermond et al., 2007). Here, the inclusion of sorption to BC significantly improves model performance, particularly for the more hydrophobic PAHs, as the deviation between measured and modeled concentrations of Pyr and BaP in the sediment reduces by approximately one order of magnitude (not shown), to only a factor of 2 (Fig. 3). The importance of BC in modeling PAHs sorption in sediment has been previously demonstrated (Hauck et al., 2007). The typical value of the fraction (0.002) of BC in aquatic sediments, which is applied in the present study, seems to be a reasonable estimation when field data are not available. In addition, it has been shown that metabolic transformation at higher trophic levels may cause trophic dilution of PAHs in aquatic food webs (Wan et al., 2007). Here, the inclusion of metabolic transformation has a significant positive effect on the outputs of PAHs concentrations in fish and invertebrates (not shown), which is crucial to model the bio-accumulation of PAHs in food web (Moermond et al., 2007). Overall, our model reconfirms the importance of incorporating the processes of BC sorption and metabolic transformation for PAH modeling (Di Paolo et al., 2010; Hauck et al., 2007; Moermond et al., 2007). On a seasonal scale, the model provides a reasonable match with the observations for the three PAHs in the gaseous phase and aerosol particles in air. However, the model shows a relatively limited ability to predict seasonal variations of PAH concentrations in the water column (dissolved and suspended solids) (Fig. S4). More details are provided as Supporting Information. The seasonal validation improves more detail on model performance, detail that cannot be clearly demonstrated from annual average results. For example, better model performance for aerosol particles than for the gas phase can be observed from the seasonal simulation data (Fig. S4), but cannot be easily seen on an annual average scale (Fig. 3). Overall, the results imply that within short temporal scales, the developed model, with all the mechanisms above incorporated, is capable of predicting the magnitude in most compartments (less than 0.7 logarithm units deviation between measured and modeled values for five-sixths of outputs) and seasonal patterns in abiotic conditions.
compartments (air and water) for the three PAH residual concentrations within Lake Chaohu. The model was subsequently evaluated using long-term data.

3.2. Model evaluation using long-term simulation

The 60-year simulation was evaluated against data using the historical records in the sediment cores (Fig. 4). The model predictions for the sediment show a good match to the long-term historical records, whereas the prediction power in other compartments remains untested. Based on the model predictions, emission in the lake catchment (Fig. S3) drives the accumulation of PAHs in the sediment of Lake Chaohu since the 1950s, which is consistent with the positive correlations between PAH emissions and residue levels in sediments of Lake Chaohu (Ren et al., 2015). However, the model tends to overestimate the concentrations of Phe before 1990 (Fig. 4A). This discrepancy may be attributed to the underestimation of biodegradation of low-molecular-weight PAHs, the effect of which may be much stronger in earlier time. The general decreasing trend of PAHs in sediment after the 2000s is in

Fig. 3. Comparison of measured and modeled concentrations (on a logarithmic scale) of Phe (A), Pyr (B) and BaP (C) in all the model compartments averaged over the short-term simulation period. Error bars for measured data relate to standard deviation (s.d.) of monthly observations on different sample sites (May 2010 to April 2012 for water phase, and May 2010 to April 2011 for air, aerosol particles and suspended solid), or s.d. obtained from literature (other compartments). Error bars for modeled data relate to s.d. of simulation outputs. Observations in zooplankton are not available.
line with the emission data (Fig. S3), which was however not fully captured in the model outputs. Multiple factors may contribute to this deviation, such as the absence of long-term data regarding BC contents in the sediment. A better model prediction may be achieved by using time explicit data of BC content in sediment cores. This BC content may have decreased after the 2000s due to a higher energy use efficiency (Wang et al., 2014) and enhanced burial. Nonetheless, the general agreement between measured and modeled PAH concentrations in sediment with respect to both magnitude and temporal dynamics implies that long-term model simulation outputs can be used for further evaluation.

3.3. Impact of the regime shift on the modeled fate of PAHs

The regime shift in this lake was characterized by a loss of macrophytes, rapidly developing blooms of phytoplankton, a switch in fish community towards domination of small zooplanktivorous fish, a strong enhancement in sediment resuspension and a substantial increase in suspended solid concentration (Fig. S1). The lake state dynamics are nicely represented by the vegetation coverage from the PCLake model (Fig. 5A), which agrees well with the field data (Kong et al., 2017). Long-term dynamics of the mass distribution for the three modeled PAHs among various compartments are simulated for the same period (Fig. 5). In general, our modeling results demonstrate that the mass distribution of less hydrophobic PAH in the lake is more susceptible to changes in ecological structure than that of more hydrophobic PAH (Fig. 5B-D). During the clear state (1958-1962), the model shows that a large fraction of Phe in the lake area is distributed in the food web (55.6% on average), while the fractions are much lower for Pyr and BaP (2.6% and 0.3% on average, respectively). On the other hand, during the turbid state after the regime shift (1963-2012), the corresponding average values become 0.050%, 0.010% and 0.008% for Phe, Pyr and BaP, respectively, and the dominant sinks of the three modeled PAHs in the total environment of the lake catchment are soil and sediment. This finding agrees with results from indoor mesocosm experiments (Roessink et al., 2010), which show that the less hydrophobic and more mobile HOCs are more susceptible to ecological changes than the more hydrophobic and less mobile HOCs.

The model further indicates that the higher susceptibility to ecological changes for less hydrophobic chemicals is attributable to their higher tendency to get absorbed by macrophytes (Fig. 5B) before they get a chance of being adsorbed to BC. The model confirms that macrophytes are one of the dominant sinks for Phe in addition to soil and sediment in a clear lake basin, which is quantitatively in accordance with earlier results from laboratory mesocosm experiments mimicking conditions of shallow lakes (Roessink et al., 2010). In addition, the fractions of total mass in macrophytes for more hydrophobic PAHs decrease drastically with increasing molecular weight (Fig. 5B-D), resulting in a lower susceptibility to ecological changes for Pyr and BaP. Both Pyr and BaP are primarily bound in soil and sediment rather than in the macrophytes because of their stronger sorption to BC than that of Phe (Koelmans et al., 2006). Therefore, different sorption abilities to BC of chemicals determine their behaviors during regime shifts. More hydrophobic PAHs may be bound primarily to soil and sediment due to stronger BC sorption, thereby being less affected by a regime shift within biotic compartments.

As for modeling PAH bioconcentration by macrophytes, our model may leave some room for improvement. Based on previous modeling work (Janse, 2005), the equation for macrophytes (see the Supporting Information) describes the exchange of substances with water and sediment separately, whereas it ignores the transport process between root and shoot, and it considers the chemicals to be evenly distributed in the macrophyte biomass. However, recent work has shown that chemicals were more slowly translocated from root to shoot than the other way around (Diepens et al., 2014). Consequently, including heterogeneity within the

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**Fig. 4.** Comparison of measured and modeled concentrations of Phe (A), Pyr (B) and BaP (C) in sediment solids for the long term simulation (January 1953 to December 2012). Measured data are the average values from the two sediment cores, and modeled data are plotted as the annual average values of each year.
macrophytes and accounting for translocation between shoot and root in our model, may further increase ecological realism and provide more accurate simulations, especially when partitioning to macrophytes is important like during the clear state before 1963 (Fig. 5). However, parameters regarding uptake and elimination kinetics of PAH in sediment-rooted macrophytes are still uncertain and scarce (Diepens et al., 2014). More field data, as well as a more comprehensive submodel for macrophytes involving heterogeneity, are expected in future research.

The capacity of macrophytes to store considerable amounts of PAHs, i.e. ‘biomass dilution’ (Roessink et al., 2010), results in the depletion of PAHs in other environmental compartments, most importantly in biota. The model shows that in a clear lake, macrophytes account for 99.7% of Phe mass, 99.2% of Pyr mass and 83.1% of BaP mass in the water column above the sediment (Fig. 5E). Further indoor experiments have focused on investigating the potential of certain macrophytes to become a major storage reservoir for HOCs (Schneider and Nizzetto, 2012). In addition, macrophytes are modeled to stabilize the sediment, thereby reducing resuspension fluxes due to fish bioturbation and wind shear stress in shallow lakes (Janssen, 2005). Consequently, the concentrations of suspended solids and PAH in the dissolved phase are lower with macrophytes present, due to lower desorption of PAHs from the suspended solids and to higher accumulation in macrophytes. We can infer that ecological restoration of a turbid lake back to a clear, macrophyte-rich state will not only improve water quality, ecological functioning and services, but also lead to the redistribution of PAHs in the lake ecosystem where higher proportions of PAHs will end up in macrophytes. As a consequence, PAH concentrations in suspended solids and biota compartments, as well as the toxic effects and ecological risks of these contaminants, may be reduced on an annual scale.

After the lake ecosystem tips into a turbid state, the dominant sinks of the three modeled PAHs are primarily soil and sediment, whereas phytoplankton being the primary producer accumulates only a negligible fraction of PAH mass in the whole environment (Fig. 5B-D). The predominant roles of soil and sediment to determine PAH distribution in an aquatic ecosystem are in agreement to earlier studies (Liu et al., 2007; Roessink et al., 2010). However, within the water column above the sediment (the soil and sediment compartments were both excluded), the model reveals the significant role of phytoplankton in the distribution of PAHs, particularly for more hydrophobic chemicals such as Pyr and BaP, because 39.7% of Pyr mass and 83.8% of BaP mass are associated with the phytoplankton (Fig. 5F). A similar pattern was observed in an earlier laboratory study, in which periphyton dominated the mass distribution of PAHs in indoor model ecosystems when macrophytes were not present (Roessink et al., 2010). This effect also has been recognized for pelagic ecosystems (Nizzetto et al., 2012), in which phytoplankton is referred to as the ‘biological pump’ (Jurado and Dachs, 2008). PCLake shows that biomass of phytoplankton is much higher without macrophytes (Fig. S1), primarily due to the increase of available nutrients from the dead macrophytes and the destabilized sediment. The rapidly increased phytoplankton biomass may bind large amounts of PAHs from the dissolved phase, which may promote the transfer of PAH from the atmosphere to the water as was suggested before (Dachs et al., 1999). In addition, the mortality of phytoplankton may enhance the vertical flux to sediment, whereas the absence of macrophytes may also result in a higher resuspension intensity. Consequently, the interaction between water and sediment possibly is much stronger in turbid than in clear lakes, which may enlarge the pool of sediment acting as a sink of PAHs. Our study reveals that the capacity of phytoplankton as a storage reservoir of PAHs is much

Fig. 5. Long term model simulations from 1953 to 2012. (A) Vegetation coverage from field observations (red dots) and PCLake model simulation (black line) (from Kong et al., 2017), which indicates the lake state (clear or turbid); (B-D) Modeled chemical mass fractions for Phe (B), Pyr (C) and BaP (D) among various compartments in the lake area. (E and F) Modeled average relative mass distributions of Phe, Pyr and BaP in water, suspended solids and all the biota compartments in the food web during the periods of clear (1958-1962, E) and turbid (1980-2012; F) states (note that soil and sediment are not included). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
lower than that of macrophytes, but the influence of phytoplankton on the fate of PAHs in the components of the food web and the aqueous phase can be substantial.

3.4. Integrated modeling approach: merits and limitations

The model developed in the present study has several advantages over earlier models. By forcing the contaminant fate model with outputs from the PClake ecosystem model, our model accounts for processes including organic carbon cycling, transport and accumulation of PAHs in the foodweb, and limnologic processes such as bottom up and top down control, which are essential to evaluate the fate of contaminants in lake ecosystems with changing nutrient loading (Koelmans et al., 2001). In addition, long-term and intensive time series data from field observations in lake ecosystems are usually scarce, particularly those covering a time span where regime shifts occur. Complex aquatic ecosystem models describing the main biotic and abiotic components, such as PClake, can be considered as a ‘virtual mesocosm’, the output of which can subsequently serve as the supplement of sparse field observations. Our model may provide benefits for lake management, for instance to base a trigger for sediment PAH remediation on anticipated consequences of abatement of eutrophication, which in part have been covered at length in earlier literature (Koelmans et al., 2001).

The toxic effect of PAHs on organisms was assumed to be negligible here, because observed PAH concentrations are below the PEC levels (Fig. S2). Here the thresholds for PAHs (TEC and PEC) are both consensus-based sediment quality guidelines for freshwater ecosystems (MacDonald et al., 2000). This, however, may not be true in other cases. After all, PClake predictions without accounting for the toxic effects may be biased because toxicity may affect abundances of certain sensitive species (e.g. arthropods), which play key roles in food web interactions (Koelmans et al., 2001). Including the toxic effect of PAHs in the model would permit to investigate if high PAHs concentrations could trigger regime shifts on the ecosystem level. Like all other ecological stressors, toxicity of HOCs is known to cause gradual changes on the level of individuals (e.g. impairment of individuals), populations and communities (e.g. the abundance and diversity of species) (Diepens et al., 2016). Several studies have further indicated adverse effects of chemicals, e.g. tributyltin and organochlorine pesticides, that break down the feedback mechanisms that promote the dominance of macrophytes (Sayer et al., 2006; Stansfield et al., 1989). The possibility of HOCs to cause regime shifts in lakes may largely depend on the systems’ stability, i.e. how far the system is from the tipping point, which is generally determined by multiple factors, such as food web interaction, trophic state and chemical pollution.

4. Conclusion

We provided an integrated ecological and BC-inclusive chemical transport and food web accumulation model, which predicted concentrations of three different PAH compounds that are consistent with short-term and long-term measured data. Model simulations revealed a full picture of the impact of demonstrated regime shifts in the shallow lake ecosystem on the fate of the PAHs. Also for the first time, historical records from sediment cores were used for model evaluation, serving as an alternative way to compensate data deficiency. The model revealed that regime shifts in shallow lakes have a stronger impact on the fate of less hydrophobic compounds than on more hydrophobic compounds due to the large storage capacity of macrophytes, which in the studied case accumulated up to 55.6% of Phe in the clear state. The abrupt disappearance of macrophytes after the regime shift resulted in a sudden change in Phe distribution. For more hydrophobic compounds such as BaP, the impact of the regime shift was negligible for the whole environment, yet large for biotic components. The present study demonstrates how integrated modeling can assist in identifying the central roles of both abiotic components (soil and sediment) and biota at the base of the food web (phytoplankton and macrophytes) in driving the distribution of PAHs in shallow lakes.

The present results may have implications for lake management, as many shallow lakes around the globe are simultaneously polluted by excess nutrient loads and HOCs such as PAHs. A better understanding of their interactions may enhance our prediction power on the fate of HOCs, which in turn may facilitate the development of sound lake management strategies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2017.04.042.

References


