

Predicting seasonal fate of phenanthrene in aquatic environment with a Markov chain

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Abstract Phenanthrene (Phe) with carcinogenicity is ubiquitous in the environment, especially in aquatic environment; its toxicity is greater. To help determine toxicity risk and remediation strategies, this study predicted seasonal fate of Phe in aquatic environment. Candidate mechanisms including biodegradation, sorption, desorption, photodegradation, hydrolysis and volatility were studied; the results for experiments under simulated conditions for normal, wet and dry seasons in the Yinma River Basin indicated that biodegradation in sediment, sorption, desorption, and volatility were important pathways for elimination of Phe from aquatic environment and showed seasonal variations. A microcosm which was used to mimic sediment/water system was set up to illustrate seasonal distribution and transport of Phe. A Markov chain was applied to predict seasonal fate of Phe in air/water/sediment environment, the predicted results were perfectly agreed with results of microcosm experiments. Predicted results with a Markov chain suggested that volatility and biodegradation in sediment were main elimination pathways, and contributions of elimination pathways showed seasonal variations; Phe was

eliminated from water and sediment to negligible levels over around 250 h in August and over 1000 h in May; in November, Phe was eliminated from water to a negligible level while about 31 % of Phe amount still remained in sediment over 1000 h.

Keywords Phenanthrene · Aquatic environment · Seasonality · Fate · Markov chain · Microcosm

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an ubiquitous group of persistent organic pollutants (POPs) in the environment, there are 16 PAHs in U.S. Environmental Protection Agency (USEPA) priority list due to their teratogenicity, mutagenicity and carcinogenicity, and phenanthrene is one of them (Wang et al. 2009; Frapiccini and Marini 2015). Despite PAHs posing a toxicity risk to human health and environment in many cases (Snip et al. 2014), only total PAHs and Benzo(a)pyrene in aquatic environment are retained within standard quality assessments by the Ministry of Health of the People's Republic of China (Sun et al. 2015a, b; MHPRC 2007). Phenanthrene (Phe) with carcinogenicity is in the presence of different environmental compartments, including sediment, water, and particulate air, mainly through combustion of coal, petroleum, wood and wastewater treatment (Shen et al. 2009). To determine toxicity risk and remediation strategies, not only toxicity assessment of Phe in aquatic environment should be implemented but also the knowledge on the environmental fate is quite necessary (Zhu et al. 2007).

Candidate mechanisms for the fate of trace organic compounds in aquatic environment include biodegradation, sorption, desorption, photodegradation and volatility (Dong et al. 2015; Zoppini et al. 2016; Olshansky et al. 2011; Gan et al.

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2014; Mead et al. 2014). Biodegradation is a natural attenuation process for organic compounds in aquatic environment (Gupta et al. 2015). Aquatic sediment often acts as a long-term reservoir for hydrophobic organic compounds (HOCs), and under anoxic conditions, microorganisms can degrade organic compounds into substances with less toxicity and less tendency to bioaccumulation (Zanaroli et al. 2015). Sorption and desorption of HOCs are considered as other major mechanisms, as HOCs have a great tendency of sorption onto sediment due to their natural characteristics of high hydrophobicity, and their desorption from sediment into water can release secondary contamination (Cheng et al. 2015; Zhang et al. 2014; Poot et al. 2014; Sun et al. 2010). In sunlight water, photodegradation of organic compounds is an important natural attenuation process, and the significance of photodegradation is quite essentially assessed when refining the toxicity risk assessment of organic pollutants (Li et al. 2014; Vione et al. 2009). Apart from these mechanisms, hydrolysis may influence fate of organic compounds in aquatic environment (Koumaki et al. 2015).

Being a HOC, Phe undergoes a range of transport and transformation mentioned above in aquatic environment (Loos et al. 2012). To reflect attenuation processes, and synthesize the roles of transport and transformation in a lake or river system, a well-established model, a Markov chain was employed (Saloranta et al. 2008; Gronewold et al. 2009). A Markov chain is a stochastic process theory, which can evaluate the chance for one state transferring into another through one or more steps at a certain time interval (Zhu et al. 2007). In the environmental research, a Markov chain has been applied to evaluate the transport of pollutants along the food chain in an ecological system and predict concentration levels of pollutants in indoor air (Zhang and Dai 2007; Nicas 2000). To our best knowledge, only one study is concerned on the application of a Markov chain to predict the fate of chemicals in aquatic environment. Zhu et al. predicted the fate of Nitrobenzene in aquatic system with Markov chain (Zhu et al. 2007). So far, the research on the application of a Markov chain to predict the environmental fate of chemicals has been still limited. In addition, the seasonal effects on mechanisms for transport and transformation, such as biodegradation and volatility, can result in seasonal variation in the fate of organic compounds in aquatic environment (Robles-Molina et al. 2014); however, few studies have focused on this issue (Kong et al. 2014).

Accordingly, the objectives of this study are to evaluate mechanisms for transport and transformation based on simulation experiments, build up a microcosm to illustrate transport and distribution of Phe in sediment/water system, apply a Markov chain to predict fate of Phe in air/water/sediment environment and testify the accuracy and efficiency of application of a Markov chain to the environmental fate of chemicals. All the experiments were conducted under

simulated conditions for normal season (May), wet seasonal (August) and dry season (November) in the Yinma River Basin to clarify seasonal variation in the fate of Phe in aquatic environment. This information can be in aid of toxicity risk assessment and remediation strategies.

Materials and methods

Chemicals

Phenanthrene (Phe) with a reported purity >99.9 % was purchased from Sinopharm Chemical Reagent Co., LTD (Shanghai, China). Stock solutions of Phe were prepared by dissolving in methanol and stored in the refrigerator. Standard solutions of Phe (100 ng/mL) purchased from Sinopharm Chemical Reagent Co., LTD (Shanghai, China) were diluted, and standard curves were made to quantify the Phe concentrations. The selected physicochemical properties of Phe are presented in Table S1. All the chemical reagents used in this study are of analytical grade or higher. All the organic solvents are of chromatographic grade.

Sampling

The Yinma River Basin (43° 0' N–45°0'N, 124° 30' E–126° 0' E) is located in Jilin Province of China with distinctive seasons. May, August and November are normal, wet and dry seasons. The average temperature in May, August and November are 13 °C, 25 °C and 5 °C, respectively. A paired set of sediment and water samples was respectively collected from 14 provincial and three state monitoring sections in the Yinma River Basin in May, August and November, 2015. The water samples (each at 1 L) were collected below 0.5–1 m of surface water with a hydrophore, and the surface sediment samples (each at 1 kg) were collected with a grab sampler. Three subsamples were mixed into a composition sample, every two subsamples were far from 1 km. The locations of sampling sites were recorded with a global position system (GPS), and the samples were taken at the same location in three seasons. The sediment samples were air-dried, ground and passed through a 2-mm sieve. The sediment used in experiments was mixed with sediment samples collected from 17 sampling sites and stored in brown jars. The water used in experiments was mixed with water samples collected from 17 sampling sites. Then water was passed through 0.45 µm glass fibre filters, and a part of water was passed through 3 µm glass fibre filters, and stored under -4 °C in refrigerator. The selected properties of sediment and water collected in three seasons are represented in Tab. S2. Based on preliminary experiments, the concentrations of Phe in sediment and water used in the experiments were determined to be below the detection limits.

Simulation experiments

All the experiments were respectively conducted under controlled conditions of 13 °C in May, 25 °C August and 5 °C in November. The temperatures in the lab were controlled with air conditioners. Except for the samples used for biodegradation experiments, all the instruments, samples and deionized water used in the experiments were sterilized to avoid the loss due to biodegradation.

Sorption and desorption by sediment

Sorption The sediment (50 g) was added in a 250-mL brown glass bottle and filled with 500 ng/mL of Phe solutions prepared by stock solution dissolving in natural water. The methanol was maintained at less than 0.1 % (v/v) to minimize the effect. Then pH of solution was adjusted to 6.5 which was the pH value of the Yinma River (Table S2), and bottles were capped with eight layers of sterile gauzes tightly. The bottle was horizontally shaken on an orbital shaker at 150 rpm. Based on preliminary experiments, the sorption equilibria reached within 216 h in May, 120 h in August and 432 h in November. At determined time intervals, 1 mL of supernatant was filtered with a 0.45- μ m glass fibre filter (syringe-driven) and analyzed with high performance liquid chromatography (HPLC).

Desorption The stock solution (100 mg/L) was added to sediment to make 500 ng/g of sediment concentration (dry weight), and the sediment was left overnight. Then, 150 mL of fresh background natural water was added to the bottle and horizontally shaken under the same condition. The supernatant was removed completely by centrifuging at 2800 r/min for 20 min every 12 h, then 150 mL of fresh background natural water was added. At determined time intervals, filtered supernatant (1 mL) was sampled for HPLC analysis. The desorption experiments were repeated until Phe concentration was below the detection limit. Control and duplicated experiments were conducted at the same time.

Biodegradation in sediment

Two sediments (each at 200 g) were respectively added in Teflon-capped brown glass vials. One sediment was sterilized and the other was unsterilized. One milliliter of Phe solution (100 mg/L) was added in each vial to make 500 ng/g of sediment concentration (dry weight). Based on the results of water contents of 17 sediment samples respectively collected in May, August and November 2015; the average water contents were all around 40 %. To make similar water content of sediment from the Yinma River, 120 mL of sterilized natural water was added in sediment. All the vials were tightly capped with eight layers of sterile gauzes to create an anaerobic

environment. At specific time intervals, 2 g of sediment were collected for Phe analysis. Control and duplicated experiments were conducted at the same time.

Volatility and photodegradation in water

Volatility One liter of Phe solution (500 ng/mL) was added into a 2-L breaker. The breaker was left open to atmosphere in the dark (avoid photodegradation), and the solution was stirred at a rate of 150 rpm with a magnetic stirrer. At determined time intervals, 1 mL of solution was sampled for HPLC analysis.

Photodegradation One hundred milliliters of Phe solution (500 ng/mL) was added into a quartz Petri dish, and the dish was sealed with a quartz lid to avoid the loss of volatility. To get the most sunlight, the photodegradation experiments were conducted on the roof of the Environment Building at Northeast Normal University within the region of the Yinma River Basin. At determined time intervals, 0.5 mL of solution was sampled for HPLC analysis.

Hydrolysis A 100-mL Teflon-capped brown vial was filled with 100 mL of Phe solution (500 ng/mL) and capped tightly with eight layers of sterile gauzes. The solution was stirred at a rate of 150 rpm with a magnetic stirrer. At determined time intervals, 0.5 mL of solution was sampled for HPLC analysis.

Biodegradation Natural water used in this experiments were filtered with 3- μ m glass fibre filters. Two 250-mL Teflon-capped brown glass vials were respectively filled with 500 ng/mL of Phe solutions prepared by stock solutions dissolved in sterilized and unsterilized natural water. The vials were tightly capped to minimize the loss of volatility. The vials were agitated at 150 rpm on an orbital shaker. At determined time intervals, 0.5 mL of solution was taken for HPLC analysis.

Control and duplicated experiments were conducted at the same time.

Microcosm experiments

The sediment and natural water used in microcosm experiments were all unsterilized.

To mimic sediment/water system, we set up a microcosm which was comprised of a toughened glass tank and a pump to circulate water (Fig. 1). The height of the sediment was below the height of the inlet. Twenty kilogrammes of sediment (dry weight) were spread on the bottom of the tank. Then, natural water with 500 ng/mL of Phe concentration was filled at the same level of the outlet, and circulated at a constant water flow rate of 40 mL/min. To keep at the same water level, deionized water was added to compensate the volatilized water. At

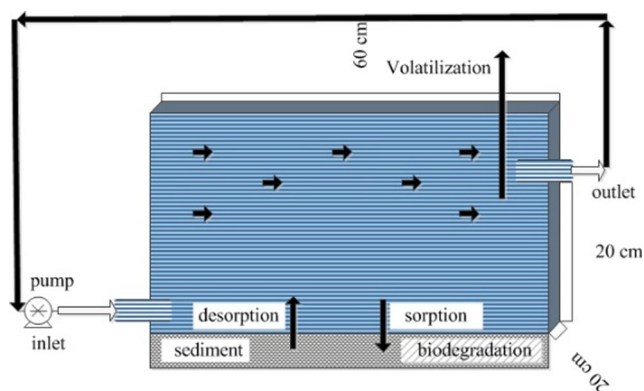


Fig. 1 Sketch of microcosm

determined time intervals, 1 mL of water and 2 g of sediment were sampled for HPLC analysis. The whole experiments were lasted for 10 days in August, 20 days in May and November.

Analysis of Phe in water and sediment

Extraction method The extraction method of Phe in sediment was followed Sun et al. (2015a, b). The sediment sample (2 g) was mixed with anhydrous sodium sulphate (1:1/w:w), and 30 mL of *N*-hexane/dichloromethane (1:1/v:v) were added. Then, the sediment was extracted in an ultrasonic bath for 30 min (repeated three times), and the extracts were reduced to about 1 mL with a rotary vacuum evaporation apparatus. After that, the extracts and 10 mL of *N*-hexane were successively passed through a silica/anhydrous sodium sulphate column, and the column was eluted with 30 mL of *N*-hexane/dichloromethane (1:1, v/v) at a constant rate of 6 mL/min under vacuum. The elutes were reduced to dryness, and Phe was dissolved with 1.0 mL of methanol for HPLC analysis. Prior to extraction, recovery rates were checked. The standard solutions of Phe (50, 100, 200, 300, 400 and 500 ng/mL) were respectively spiked with unpolluted sediments. The result recovery rates for Phe were 70–105 %, indicating that the extraction method was efficient.

HPLC analysis The concentrations of Phe in the sediment and water samples were analyzed by a HPLC system equipped with a symmetry reversed-phase C18 column (4.6 × 150 mm). Phe was detected with a fluorescence detector with an excitation wavelength of 250 nm and an emission wavelength of 364 nm. The mobile phase (isocratic) was methanol/water (80/20, v/v), and flow rate was 1 mL/min. The detection limits were below 1 ng/mL for water and below 5 ng/g for sediment.

Markov Chain

A Markov chain is a stochastic process theory, which uses transition matrix to describe a chemical's transfer among

different environmental compartments (Zhang and Dai 2007). A chemical can exist in an absorbing state or in a transient state. A chemical disappearing forever from an environment compartment is considered being in an absorbing state, while a chemical transferring from one environmental compartment into another is referred as being in a transient state, but the chance of a chemical transferring from any absorbing state to any transient state is never (Zhu et al. 2007).

A chemical in multimedia environment may transfer from one state into another state after some time, the transfer of a chemical's state is stochastic and independent of previous state; therefore, this stochastic process is a Markov chain process. Provided a chemical exists in n kinds of environmental compartments, the state space can be described as $U = (U_1 + U_2 + U_3 + \dots + U_n)$. And, the chemical has r kinds of absorbing states, the transition matrix can be expressed as following:

$$P = \begin{pmatrix} R_r \times r & O_r \times n \\ A_n \times r & T_n \times n \end{pmatrix}$$

where $R_r \times r$ is the transition matrix from absorbing states to absorbing states, the diagonal elements are 1 and others are 0; $O_r \times n$ is the transition matrix from absorbing states to transient states, the chance is never; therefore, all the elements are 0; $A_n \times r$ is the transition matrix from transient states to absorbing states, and $T_n \times n$ is the transition matrix from transient states to transient states (Zhang and Dai 2007).

Supposing a chemical transfer from one state into another state after a certain time (t_0). The amount of the chemical in any state at $t + t_0$ can be calculated as Equation (1):

$$U_{(t + t_0)} = U_{(t)} \times P$$

Results and discussion

Sorption and desorption of Phe in sediment

Sorption has a major impact on the transport of Phe as Phe has a great tendency onto sediment, and Phe desorbed from sediment into water would release secondary pollution; therefore, sorption and desorption were considered in this study (Olshansky et al. 2011; Heister et al. 2013). As shown in Fig. 2, sorption of Phe from water onto sediment showed a variation in temperature. With the temperature rising, the sorption rate was higher (Table 1), which might be due to higher intensity of molecular thermal movement at a relatively higher temperature. The percentage of remaining Phe in the water decreased very fast within 48 h in August, after fast sorption, the decrease was much slower as the sorption sites significantly reduced. In May and November, the percentages of remaining Phe in the water decreased at a relative constant rate, the rates were relatively lower.

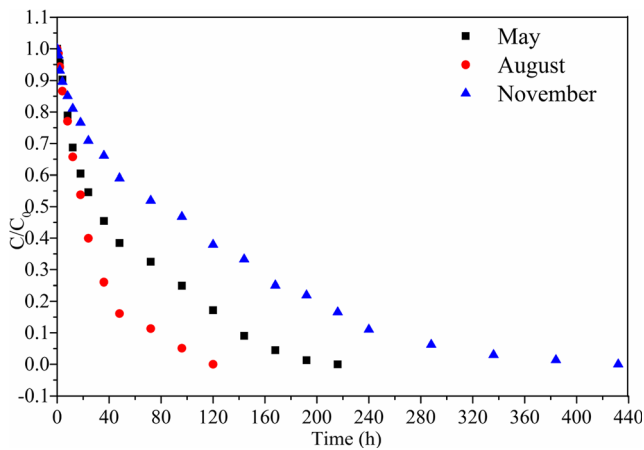


Fig. 2 Change in percentage of remaining Phe in water

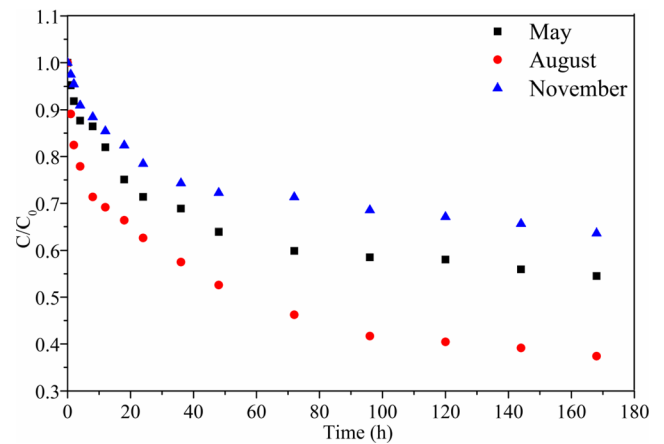


Fig. 3 Change in percentage of remaining Phe in sediment

Figure 3 indicates that desorption of Phe from sediment into water showed the same variation in temperature as sorption process. As represented in Table 1, desorption process in August was divided into three stages, the fast desorption occurred in the first 8 h, then decrease in percentage of remaining Phe in sediment was slower; after 72 h, the decrease was even much slower. Whereas desorption processes in May and November were both divided into two phases, the fast desorption occurred within 24 and 36 h, respectively, then desorption rates were much slower (Table 1).

Biodegradation of Phe in sediment

Biodegradation is one of the most important natural processes for organic chemicals’ attenuation in aquatic environment. The microorganisms dwelled in the sediment can break down biodegradable organic chemicals under anaerobic conditions (Baginska et al. 2015). The preliminary results indicated that percentages of degraded Phe in sterilized sediment were below 10 % in May and August, and below 3 % in November. The decrease in percentage of remaining Phe in sterilized sediment was attributed to irreversible sorption by sediment, but it was quite slight

and could be neglected. Under 13, 28 and 5 °C, the percentages of remaining Phe in unsterilized sediment were significantly decreased, indicating that biodegradation in sediment was an important pathway for elimination of Phe in aquatic environment. But the biodegradation rate and extent showed seasonal variations which was attributed to seasonal variations in activities and abundance of microorganisms (Xia et al. 2015).

As shown in Fig. 4, biodegradation rate and extent were the highest in August when activities and abundance of microorganisms were the highest; about 500 ng/g of Phe in sediment were completely biodegraded within 168 h. Whereas the lowest biodegradation rate and extent occurred in November, although the biodegradation experiments in November were lasted for 216 h, the percentage of biodegraded Phe in sediment was just 27.68 %, which might be attributed to few species and low activities of microorganisms at low temperature. Table 1 indicates that the biodegradation rate in May was slow at first, then biodegradation rate increased greatly; thereafter, Phe in sediment was biodegraded at a relatively low rate; In August, the biodegradation rate was quite slow initially, then biodegradation rate became much higher, whereas in November, biodegradation rate was higher at first but

Table 1 Transport and transformation rates of Phe

	May	August	November
Sorption rate of Phe from water onto sediment (ng/mL/h)	0.0186	<48 h 0.0382 >48 h 0.024	0.0099
Desorption rate of Phe from sediment into water (ng/g/h)	<24 h 0.0667 >24 h 0.0029	<8 h 0.12 8–72 h 0.0099 >72 h 0.0014	<36 h 0.0552 >36 h 0.0025
Biodegradation rate of Phe in sediment (ng/g/h)	<24 h 0.0035 24–48 h 0.0093 >48 h 0.0031	<24 h 0.0079 >24 h 0.0214	<48 h 0.0037 >48 h 0.0008
Volatility rate of Phe from water to air (ng/mL/h)	0.003	0.0216	0.0013

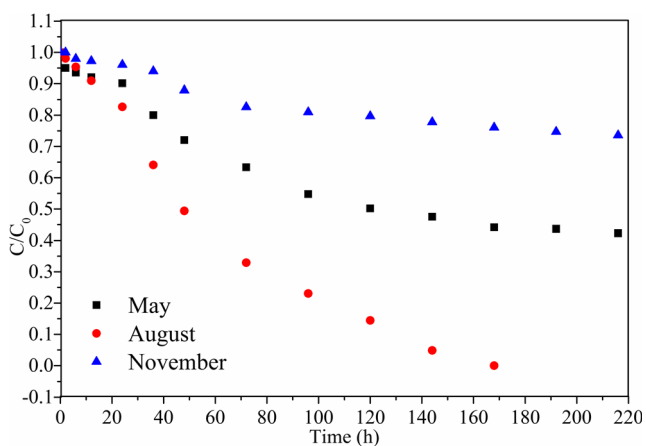


Fig. 4 Change in percentage of remaining Phe in sediment

became much lower after 48 h. In May, the slow biodegradation rate at first was due to low activities of microorganisms; with acclimation of microorganisms in sediment, the biodegradation rate became much higher. In August, with acclimation of microorganisms, biodegradation rate became higher and about 500 ng/g of Phe in sediment was completely biodegraded. In November, instead of acclimation of microorganisms at a desirable temperature over a period of time, at a low temperature the activities of microorganisms became lower after a period of time; therefore, biodegradation rate was relatively higher at first, thereafter became much lower.

Volatility, photodegradation, hydrolysis and biodegradation of Phe in water

Based on the experimental results for elimination pathways of Phe from water, the rates of photodegradation, hydrolysis and biodegradation were quite slow to be neglected, the elimination of Phe from water was primary through volatility. The volatility of Phe from water was greatly affected by temperature, volatility rate and extent increased with temperature rising. As shown in Fig. 5, volatility showed a seasonal variation, the volatility rate and extent were highest in August, about 500 ng/mL of Phe was completely volatilized from water within 216 h, whereas in November, the volatility rate and extent were the lowest, although the volatility experiments in November lasted for 336 h, the percentage of volatilized Phe from water was just 36.39 %.

Microcosm experiments

Microcosms can be applied to mimic real environment for studying transport and distribution of chemicals in environment, previous study has been reported to use a microcosm to illustrate transport and distribution of Nitrobenzene in aquatic

environment (Zhu et al. 2007; Tesoriero et al. 2001). Accordingly, a microcosm (Fig. 1) was set up to explore transport and distribution of Phe in sediment/water system. Apart from this, seasonal variations in transport and distribution were elaborated in this study.

As represented in Fig. 6, changes of Phe concentration in water and sediment microcosms were similar in three water seasons. In water, concentration of Phe decreased quickly at first, and then decrease rate became much lower. In sediment, Phe concentration initially increased greatly, and reached a maximum, then gradually decreased. In sediment/water system, initially, fast decrease of Phe concentration in water and quick increase of Phe in sediment were due to volatility and sorption onto sediment. As sorption reached equilibria with sorption sites reducing, Phe concentration in sediment reached the maximum, then Phe in sediment was desorbed into water. After that, Phe concentration kept decreasing as Phe continued to volatilize from water to air, and gradually, decrease of Phe concentration in sediment was mainly due to biodegradation with acclimation of microorganisms in sediment.

Table 1 indicates that transport and transformation rates showed seasonal variations; the rates of transport and transformation were the highest in August while the rates were the lowest in November; correspondingly, percentages and rates of Phe elimination from water and sediment were highest in August while were the lowest in November. In August, Phe was eliminated from water and sediment to negligible levels over around 200 h. In May, Phe was eliminated from water to a negligible level over around 400 h, but there still remained a small percentage of Phe in sediment after 500 h. In November, the most of Phe was eliminated from water. Although the microcosm experiments in November were lasted for 500 h, over 50 % of Phe still remained in sediment, which was primarily attributed to low activities and less abundance of microorganisms at a low temperature.

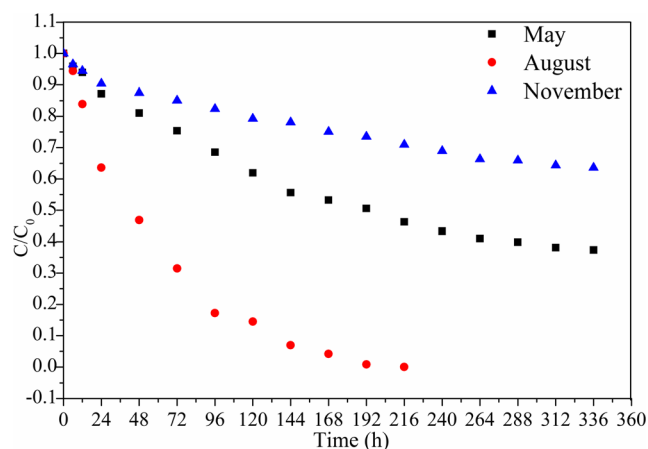


Fig. 5 Change in percentage of remaining Phe in water

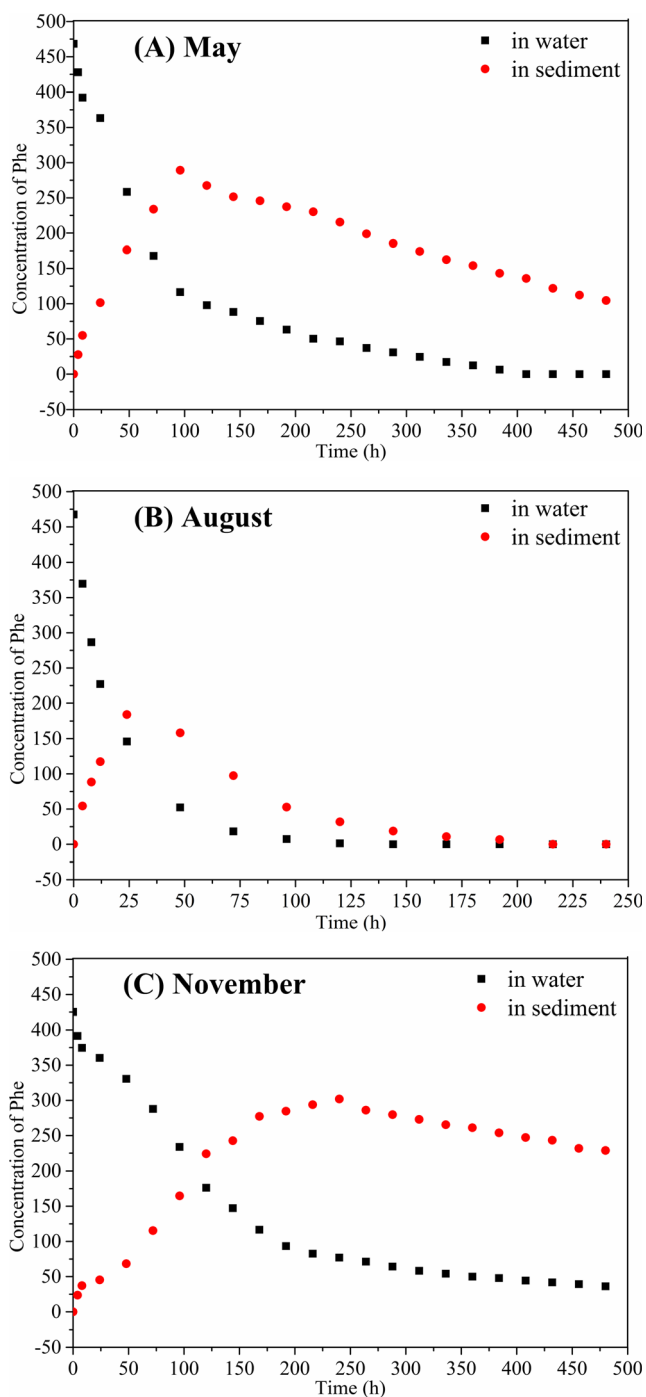


Fig. 6 Changes of Phe concentrations in water and sediment microcosms

Application of a Markov chain to environmental fate of Phe

In a Markov chain, Phe existed in three environmental compartments: air, water and sediment. Phe might disappear from the system through pathways of hydrolysis, photodegradation and biodegradation, or transfer from one environmental compartment into another through pathways of volatility, sorption and desorption. Based on experimental results, rates of

hydrolysis, photodegradation and biodegradation in water were quite low, therefore these pathways were not considered in this study.

Supposing biodegradation in sediment was state 1, volatility from water to air was state 2, Phe dissolving in water was state 3, and sorption from water onto sediment was state 4. State 1 and state 2 were considered as absorbing states while state 3 and state 4 were regarded as transient states. Phe might transfer from state 3 to state 2 or state 4. Accordingly, based on experimental data (Table 1), the transient matrix which described Phe in four states, could be expressed as section 3.5 in [Supplementary Material](#). The initial amounts of Phe were respectively 10.5 mg for May, 10.7 mg for August and 10.11 mg for November in the water, the distributions of Phe in four states for three water seasons were respectively expressed as $U(0) = (0 \ 0 \ 10.5 \ 0)$; $U(0) = (0 \ 0 \ 10.7 \ 0)$; $U(0) = (0 \ 0 \ 10.11 \ 0)$. Then, the amounts of Phe in four states over every hour were calculated with Equation (1).

Figure 7 represents the predicted changes in amounts of Phe biodegraded in sediment, in air, water and sediment over every hour. The changes in Phe amount in four states were similar in three water seasons, amount of Phe in water quickly decreased at first, then decreased at a lower rate. The amount of Phe in sediment increased fast at first, when sorption amount reached maximum, amount of Phe decreased at a lower rate. The predicted changes of Phe in water and sediment were the same as the observed changes of microcosm. In air/water/sediment environment, Phe was eliminated from water and sediment mainly through pathways of volatility from water to air and biodegradation in sediment, but contributions of elimination pathways were different in three water seasons. In May, 26 % of eliminated Phe volatilized from water to air, 74 % was biodegraded in sediment. In August, 48 % volatilized from water to air, and 52 % was biodegraded in sediment. In November, 41 % of eliminated Phe volatilized from water to air and 59 % was biodegraded in sediment. In addition, with temperature rising, biodegradation and volatility rates increased; correspondingly, elimination rates and extents of Phe from water and sediment were highest in August, and the lowest in November. In May, Phe was completely eliminated from sediment and water to negligible levels over 1000 h; in August, over around 250 h, Phe was eliminated from water and sediment to negligible levels; in November, the most of Phe was eliminated from water; however, there was still about 31 % of Phe remaining in sediment over 1000 h.

To testify accuracy and efficiency of application of a Markov chain to predict fate of Phe in aquatic environment, the predicted data were compared with observed data. As represented in Fig. 8, in three water seasons, the predicted changes of Phe concentrations in water and sediment were all perfectly fitted with observed changes of Phe concentrations in water and sediment microcosms. In addition, Pearson’s

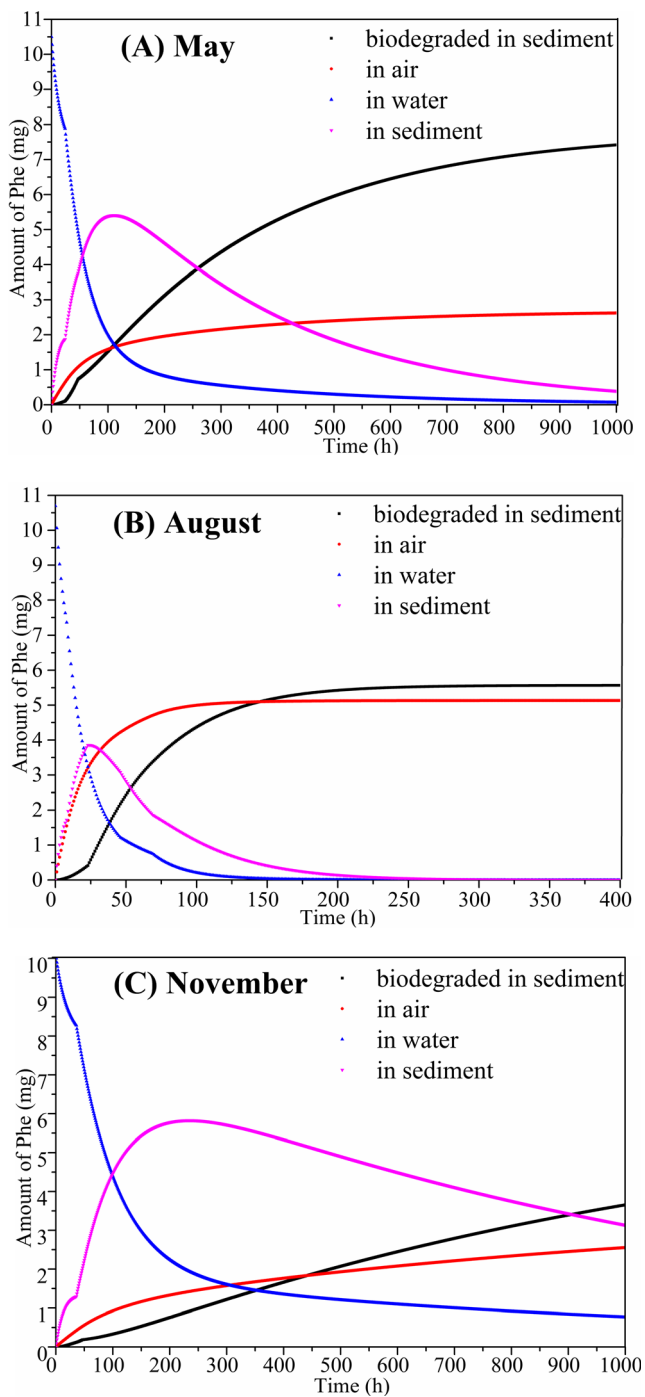


Fig. 7 The predicted changes in amounts of Phe biodegraded in sediment, in air, water and sediment with a Markov chain

correlation coefficient was applied to testify the accuracy and efficiency. As shown in Fig. S1, Pearson's correlation coefficients for water and sediment in three water seasons were all higher than 0.99, indicating that the predicted concentrations with Markov chain were perfectly agreed with observed concentrations in water and sediment of microcosm. Therefore, application of Markov model to predict seasonal fate of Phe in aquatic environment is efficient and accurate.

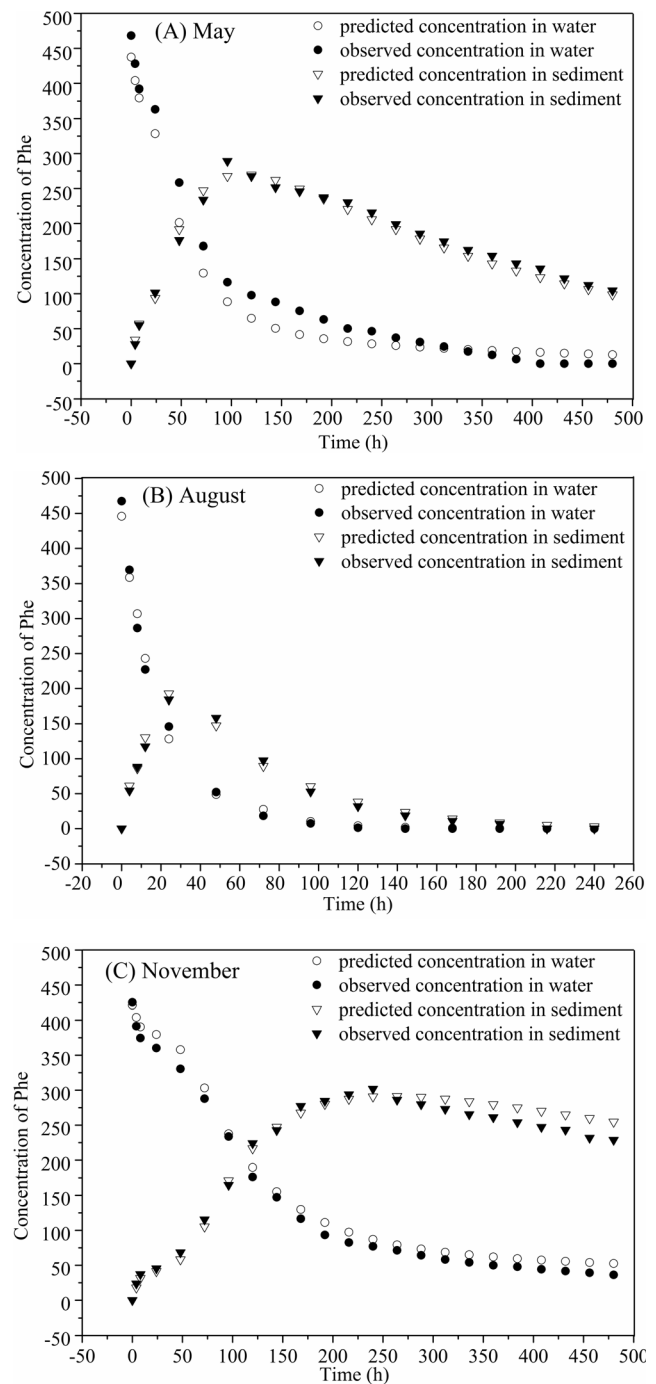


Fig. 8 Comparison of predicted concentrations of Phe in water and sediment with observed concentrations of Phe in water and sediment microcosm

Conclusions

This study predicted seasonal fate of Phe in aquatic environment. Candidate mechanisms including volatility, photodegradation, hydrolysis, degradation, sorption and desorption were investigated. The results of simulation experiments indicated that volatility, degradation in sediment,

sorption and desorption were primary pathways for transport and transformation; the rates were the highest in August while lowest in November. A microcosm was set up to illustrate seasonal distribution and transport of Phe in sediment/water system. A Markov chain was applied to predict seasonal fate of Phe in air/water/sediment environment. The predicted results were perfectly agreed with the observed results of microcosm experiments, indicating high accuracy and efficiency in the application of a Markov chain to predict environmental fate of Phe. The predicted results suggested that Phe was eliminated from sediment and water to negligible levels over around 250 h in August and over 1000 h in May; in November, over 1000 h Phe was eliminated from water to a negligible level, but about 31 % of Phe amount still remained in sediment.

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