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Distribution and fate of nonylphenol in an aquatic microcosm

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ABSTRACT

An aquatic microcosm consisting of four compartments, namely surface microlayer (SM), water sediment and biota (zebra fish), was developed to investigate the distribution and fate of nonylphenol (NP) in an aquatic environment. Level III and level IV fugacity-based multimedia models were used to calculate the distribution and fate of NP. Data obtained from model calculations were in good agreement with those of the experiments. Results of the model calculations showed that 86.50% of all NP input was removed by advective outflow, while 61.99% of the remainder was distributed to the sediment phase, 34.89% to the water phase, 2.50×10^{-2}% to SM and 3.13% to the biotic phase. This finding demonstrates that sediment plays a key role in the fate of NP and acts as a sink in the aquatic environment. Bioconcentration factor (BCF) of NP in the zebra fish was high and varied in different parts of the fish. The highest BCF was 1440 in the viscera. After the uptake experiment, depuration of NP in clean water indicated that, the concentration of residue NP in the zebra fish was still high. This implies that NP in fish can pose a potential threat to human health due to its bioaccumulation in the food chain.

1. Introduction

Nonylphenol (NP), one of the common metabolites of widely used nonionic surfactant NP polyethoxylates (NP_nEO), is more persistent and toxic than its parent substance and acts as an environmental endocrine disrupter (EDC), which has been proven by many studies (Stephanou and Giger, 1982; Jobling et al., 1996; 1998; Gray and Metcalfe, 1997; Comber et al., 1993; Yadetie and Male, 2002; Hemmer et al., 2002). NP is ubiquitous in the natural environment and has been detected in different environmental media (Bennie, 1999; Ying et al., 2002) and food (Guenther et al., 2002; Casajuana and Lacorte, 2004). Degradation of NP under aerobic and anaerobic conditions with different bacteria has been reported (Staples et al., 1999; Tanghe et al., 1998; Maguire, 1999; Körner et al., 2000; Banat et al., 2000; Topp and Starratt, 2000; Yuan et al., 2004).

It is well known that organic compounds have the ability to transfer among sediment, water and biota compartments in an aqueous system in accordance with their physical–chemical properties, influenced also by environmental conditions. Full understanding of the equilibrium partitioning and kinetics of transfer, partitioning and processing (reaction/degradation) of NP between and within aqueous compartments is important to accurately develop and calibrate models that predict the fate of NP in an environmental system (Wilson and Meharg, 1999). Model ecosystem (micro- and mesocosm) offers the possibility to study the influence of contaminants on the environment under controlled

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conditions. Microcosm studies are very important for estimating the effects of environmental pollutants, as well as direct and indirect effects (Höss et al., 2004).

The Mackay-type multimedia environmental models is an elegant approach to determine the fate of chemicals in the environment. Such models are developed based on the fugacity concept, thermodynamic equilibrium and mass balance principles. This kind of models is referred as fugacity models. There are four basic types: Level I (steady-equilibrium state, no reaction, input and output); Level II (steady-equilibrium state with reactions, input and output); Level III (steady-non-equilibrium state, different fugacities); Level IV (unsteady-non-equilibrium state, df/dt is not equal to zero, different fugacities).

Fugacity models have been successfully used worldwide to describe the behavior and fate of toxic organic chemicals (micro-pollutants) in the environment. Level IV models are most suitable in the characterization of the transport, transformation and fate of micro-pollutants in the environment. There are many successful application examples of fugacity models, such as the Quantitative Water Air Sediment Interaction (QWASI) model used for the elucidation of organic and inorganic chemical transport in lakes (Mackay and Diamond, 1989; Southwood et al., 1999); CHEMCAN model combined with GIS technique used to assess the fate of micro-pollutants in Canada (Woodfine et al., 2002); and multi-segment fugacity models used to describe the behavior and fate of lindane and benzo(a)pyrene in the Rihand Reservoir in India (Warren et al., 2002).

The fugacity approach is an elegant and simple method, which only requires the physical and chemical properties of the micro-pollutants and the environmental parameters. Model calculation is simple and can easily be implemented using computer as a calculating aid. Extensive chemical analyses for the micro-pollutants are not required, and, thus, can save money and time. Transport, transformation and degradation rates of the chemicals can be compared using the dynamic and equilibrium parameters of the model. From this, the dominant change process of the micro-pollutants can be determined and a reasonable explanation for the model output can also be obtained. Multimedia fugacity models are now routinely used for evaluating chemicals before and after production, for predicting the ultimate fate and possible adverse effects of the micro-pollutants in our total multimedia environment; as a decision-support tool in environmental management and contamination control; for contamination exposure assessment and risk assessment, as well as for the optimum design of environmental monitoring and biota monitoring.

There are two major limitations of this type of models: (1) they are only applicable if all phases can be assumed to be homogeneous; and (2) transformation and degradation processes are assumed to be first-order.

To study the distribution and fate of NP in an aquatic environment, experiments in a simulated microcosm were performed. A four-compartment (containing surface microlayer (SM), water, sediment and biota (zebra fish)) microcosm was established to simulate the aquatic environment, and level III and level IV fugacity-based multimedia models have been used to predict the distribution and fate of NP in the aquatic environment. At the same time, the concentrations of NP in different parts of the biota were measured and compared. The depuration diagram of NP in biota was plotted when the polluted biota were put into clean fresh water.

2. Experimental methods

2.1. Materials and chemicals

Sediment used in the microcosm was collected from surface soil of a garden of Nankai University, Tianjin, China. The sediment was air-dried and grasses and small rocks were removed. The properties of the sediment were determined using the standard methods used in China (Nanjing Institute of Soil Science of Chinese Academy of Science, 1978). The characteristics of the sediment are listed in Table 1.

Water was dechlorinated prior to use. Zebra fish was purchased from the market. The fish were sterilized by 5% sodium chloride (NaCl). The zebra fish were acclimatized for 2 weeks before the experiment and their death rate was below 1% during the acclimatization period.

NP (technical grade) was purchased from Tokyo Chemical Synthesis Ind. Co. Ltd., Japan. Isopropanol, *n*-hexane and methanol were HPLC grade, dichloromethane (DCM), NaCl and anhydrous sodium sulfate (Na_2SO_4) were analytical grade. Na_2SO_4 was baked at 450 °C overnight and stored in a glass desiccator before use (Shang et al., 1999). Waters Oasis® HLB cartridge (Waters Company, USA) was used for solid-phase extraction (SPE).

2.2. Microcosm establishment

The microcosm consisted of an aquarium (70 cm long × 37 cm wide × 40 cm high, sterilized with 1% potassium hypermanganate ($KMnO_4$) solution before use), with its schematic diagram shown in Fig. 1. Prior to use, the aquarium was scrupulously cleaned with a cleaning agent (chromic acid cleaning mixture). 8.4 kg sediment was homogenously placed on the bottom of the aquarium to form a 2-cm sediment layer. Water was slowly delivered into the aquarium with an initial water volume of 90.6 l; the water level was maintained at 34.7–35.3 cm (89.9–91.4 l) throughout the experiments. Inside the aquarium, there were a heater and a thermometer to maintain the temperature at 24 ± 0.5 °C; an aeration pipe with a popple device was used for aeration. White fluorescence light (2400 Lux) was installed on the top of the aquarium; light:dark ratio was 12:12. Inflow rate of water was approximately 0.9 l h^{-1}. After the microcosm was established, 20 mg of NP was spiked into the microcosm and was allowed to equilibrate for 2 days. The acclimatized zebra fish were then put into the microcosm to start the experiment.

The zebra fish were not fed during the whole experiment in order to avoid the experimental error from the food chain. The average length of zebra fish was 4.32 cm, and the average weight slightly decreased from 0.699 g/10 fish to 0.643 g/10 fish in spiked microcosm during the experiment. The average weight slightly decreased from 0.703 g/10 fish to 0.679 g/10 fish in control microcosm. The weight loss was 0.024 g/10 fish in control microcosm and 0.056 g/10 fish in spiked microcosm.

Table 1 – Selected physical and chemical characteristics of the sediment

Sediment color	Collection depth	Sediment categories	Content of organic carbon (%)	pH	Density ($g\,cm^{-3}$)
Yellowish brown	0–20 cm	Arenaceous soil	1.07	7.86	1.59

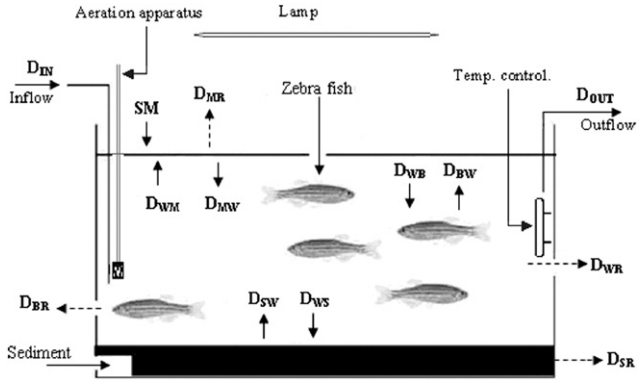

Fig. 1 – Schematic diagram of the aquatic microcosm and the transport and transformation processes of NP.

Ashfield et al. (1998) found that the weight loss of rainbow trout was about 2 g/1 fish after an exposure of 180 days to NP ($1\,\mu g\,l^{-1}$). Thus, the weight loss of zebra fish in spiked microcosm despite no feeding during the experiment might also be a consequence of the toxic effect of NP on zebra fish. The pH of the water in the aquarium was between 6.59 and 7.19, and the dissolved oxygen (DO) concentration was between 7.40 and $8.26\,mg\,l^{-1}$. Blank experiments were performed using control microcosm without NP spiking. The setup of microcosm was the same as that of the microcosm spiked with NP (see Fig. 1).

2.3. Sample collection, pretreatment

SM samples were collected using a glass plate (Harvey and Burzell, 1972; Hardy et al., 1985; Chi and Huang, 2002). The thickness of SM was 60–80 μm. The water samples were pretreated by SPE (Hou et al., 2006). The collection method of water samples was given by Chi and Huang (2002). Sediment samples were collected using a Pyrex glass pipe with a diameter of 2.0 cm. Biotic samples (10 fish) were randomly collected from the 200 fish. Sampling time was set at 0, 2, 12, 24, 48, 96, 144, 192, 240, 288, 360 and 408 h.

The sediment samples were pretreated as follows: they were centrifuged at 4000 r/m for 10 min, then the upper water was discarded and the residue was freeze-dried in a freeze-drier (ALPHR 1–2 LD, Martin Christ Gefriertrocknungsanlagen GmbH, Germany) for 24 h. Two to five grams of dried sediment samples were Soxhlet extracted with DCM as given by Lee et al. (1997). Before injection, the pretreatment of samples collected from control microcosm was the same as that of samples collected from the spiked microcosm.

The randomly collected zebra fish were wiped with filter paper, and then freeze-dried. The dried samples were weighed and put into a glass mortar, mixed with 5.0 g sodium sulfate. Then the mixture was grinded into powder. The mixture powder was packed with filter paper, and then Soxhlet extracted for 24 h. The clean-up procedure was applied as given by Huang et al. (2005), and the liquid phase was treated with SPE as given by Hou et al. (2006).

2.4. Chemical analysis

Separation was performed on a Waters 1525 HPLC with a Waters 2475 scanning fluorescence detector (set at 233 nm excitation/302 nm emission) equipped with a Waters W2108N007 NH_2 column (10 μBondapak 3.9 mm i.d. × 300 mm). A guard column (8 mm i.d. × 18 mm, packed with the same material as the analytical column) was used in-line with the analytical column. Components of the mobile phase were n-hexane/isopropanol (98/2, v/v) [A] and isopropanol/water (98/2, v/v) [B]. Flow rates in all cases were $1.0\,ml\,min^{-1}$. Calibration was performed by serial dilution of a stock solution with a nominal NP concentration of $2.0\,mg\,ml^{-1}$ in hexane. Injection volume was 20 μL. Linear gradient elution was used as follows: initial conditions: 95% A and 5% B; linearly changed to 80% A and 20% B in 10 min; kept isocratic for 5 min. Good recoveries were obtained for NP in water/SM (93 ± 4%), in the sediment (99 ± 5%) and in the zebra fish (83 ± 5%). Good reproducibility of determination was also obtained for NP in water/SM (relative standard deviation, RSD = 1.8%, $n = 5$), in the sediment (RSD = 2.3%, $n = 8$) and in the zebra fish (RSD = 1.9%, $n = 4$). Detection limit (S/N = 3) was $0.01\,\mu g\,l^{-1}$ for water and $0.001\,mg\,kg^{-1}$ for sediment and biota.

2.5. Fugacity approach

The fugacity-based model used in this study was developed based on Mackay (2001). Briefly, fugacity, f, is identical to the partial pressure of ideal gases and is logarithmically related to chemical potential. We can replace the equilibrium criterion of chemical potential by that of fugacity. Fugacity is linearly related to concentration by the equation

$$C = Zf, \tag{1}$$

where Z is the fugacity capacity. The Z values in different environmental media were given by Mackay (2001). The Z values can be calculated from partition coefficients, information on the nature of the media and the physical chemical properties (see Table 2). The rate, $N\,mol\,h^{-1}$, of transport and transformation processes of a substance of interest can be expressed as Df, where D are transport parameters with units of $mol\,Pa^{-1}\,h^{-1}$. The D values are given in Table 3.

Table 2 – Volume, density and fugacity capacity (Z) of NP of each phase in the microcosm

Phase	Volume (m^3)	Density ($kg\,m^{-3}$)	Fugacity capacity ($mol\,m^{-3}\,Pa^{-1}$)	Comment
Water	9.06×10^{-2}	1.00×10^{3}	$Z_w = 1/H = C^s/P^s = 0.0805$	$H = P^s/C^s = 12.4$ ($Pa\,m^3\,mol^{-1}$)[a]
Surface microlayer (SM)	1.85×10^{-5}	1.00×10^{3}	$Z_M = F/H = 0.281$	$F = 3.48$[b]
Sediment	5.18×10^{-3}	1.59×10^{3}	$Z_S = K_{SW}\rho_s/H = 3.61$	$K_{SW} = 28.10$ ($l\,kg^{-1}$)[b], $\rho_s = 1.59$ ($kg\,l^{-1}$)[b]
Biota (zebra fish)	4.53×10^{-5}	2.98×10^{2}	$Z_B = K_{BW}\rho_B/H = 13.1$	$K_{BW} = 540$ ($l\,kg^{-1}$)[b], $\rho_B = 2.98 \times 10^{-1}$ ($kg\,l^{-1}$)[b]

[a] P^s obtained from Nielsen et al. (2000) and C^s obtained from Ahel and Giger (1993a).
[b] Data-obtained experiments.

Table 3 – Calculation of D parameters

Parameter	Calculation of D	D values ($mol\,Pa^{-1}\,h^{-1}$)
Water inflow, D_{IN}	$D_{IN} = G_{IN}Z_W$	7.73×10^{-5}
Water outflow, D_{OUT}	$D_{OUT} = G_{OUT}Z_W$	7.73×10^{-5}
Water-to-sediment diffusion, D_{WS}	$D_{WS} = 1/(1/K_{WS}A_SZ_W + Y_S/B_SA_SZ_s)$	8.79×10^{-5}
Sediment-to-water diffusion, D_{SW}	$D_{SW} = D_{WS}$	8.79×10^{-5}
Water-to surface microlayer diffusion, D_{WM}	$D_{WM} = K_{WM}A_MZ_M$	5.77×10^{-6}
Surface microlayer-to-water diffusion, D_{MW}	$D_{SM} = D_{WM}$	5.77×10^{-6}
Water-to-biota diffusion, D_{WB}	$D_{WB} = K_{WB}V_BZ_B$	1.43×10^{-5}
Biota-to-water diffusion, D_{BW}	$D_{BW} = D_{WB}$	1.43×10^{-5}
Water transformation, D_{WR}	$D_{WR} = K_{WR}V_WZ_W$	6.02×10^{-6}
Surface microlayer transformation, D_{MR}	$D_{MR} = K_{MR}V_MZ_M$	4.29×10^{-9}
Sediment transformation, D_{SR}	$D_{SR} = K_{SR}V_SZ_S$	5.40×10^{-6}
Biota transformation, D_{BR}	$D_{BR} = K_{BR}V_BZ_B$	7.83×10^{-8}

Partition coefficients: $K_{SW} = 9.32 \times 10^{1}$ ($m\,h^{-1}$)[b]; $K_{MW} = 7.93 \times 10^{-5}$($m\,h^{-1}$)[b]; $K_{BW} = 2.41 \times 10^{-2}$($h^{-1}$)[c1]; $Y_S = 1.5 \times 10^{-2}$ (m)[a]; $G_I = 9.6 \times 10^{-4}$($m^3\,h^{-1}$)[b]; $G_O = 9.6 \times 10^{-4}$($m^3\,h^{-1}$)[b]; $K_{WR} = 8.25 \times 10^{-4}$($h^{-1}$)[c2]; $K_{MR} = 8.25 \times 10^{-4}$($h^{-1}$)[c2]; $K_{SR} = 2.89 \times 10^{-4}$($h^{-1}$)[c3]; $K_{BR} = 1.32 \times 10^{-4}$($h^{-1}$)[c1]; [a]data obtained from Mackay (2001) and Chi and Huang (2002); [b]data obtained from experiments; [c]data obtained from references; [1]Chen (1998); [2]Ekelund et al. (1993); [3]Ferguson et al. (2001). G_I and G_O denote inflow rate and outflow rate, respectively. As: interface area of water–sediment (m^2); Y_s: average diffusion depth (m); B_s: effective coefficient of pore–water ($m^2\,h^{-1}$).

3. Results and discussions

3.1. *Distribution and desorption of NP in multimedia*

3.1.1. *Water and SM*

Fig. 2(a) shows the trends of NP concentration in water and in the SM of the aquatic microcosm. As soon as the NP was added into the microcosm, it dispersed into the various media. It was observed that the concentration of NP in water decreased with time. At 5 h, the concentration was the lowest ($0.041\,mg\,l^{-1}$ as shown in the inset figure of Fig. 2(a)). Then, it fluctuated to reach a steady value of $0.055\,mg\,l^{-1}$ after 144 h. On the other hand, the concentration of NP in the SM increased quickly at the beginning of the experiment to $0.40\,mg\,l^{-1}$. This corresponds to a concentration factor (CF) of 7.27, which is defined as the concentration of NP in the SM at time t divided by the water concentration at t. After 6 h, the concentration of NP decreased slowly and reached a constant value of $0.13\,mg\,l^{-1}$. At 96 h, the CF became 2.36. This decrease in CF from 7.27 to 2.36 from the beginning to a steady state in the SM can be explained as follows. When the zebra fish were first introduced into the microcosm, the concentration of suspended particulate matter (SPM) also increased considerably, which resulted in a higher CF at the beginning of the experiment. As the concentration of SPM decreased and became constant, the CF decreased to a lower value.

3.1.2. *Sediment*

Concentration variation of NP in sediment is shown in Fig. 2(b). At the beginning of the experiment, the concentration of NP in sediment increased, which can be attributed to the high adsorption rate of NP on sediment. As part of the NP adsorbed on the surface of sediment desorbed, the con centration of NP in sediment decreased gradually. Then, it eventually reached a steady state after 240 h. The concentration of NP in sediment became $1.02\,mg\,kg^{-1}$ at 240 h. Bennie (1999) reported that the concentrations of NP in sediment were no more than $72\,mg\,kg^{-1}$. The overall average K_d ($= C_s/C_w$) value of NP in the current study was $28.10\,L\,kg^{-1}$, which is far smaller than those reported in other studies, such as $4.54 \times 10^{3}\,L\,kg^{-1}$ (Li et al., 2004) and $2.94 \times 10^{2}\,L\,kg^{-1}$ (Bolz et al., 2001). Khim et al. (1999) reported on NP concentration ranging from 20.2 to $1820\,ng\,g^{-1}$ dry wt in Shihwa Lake sediments. This high concentration was the

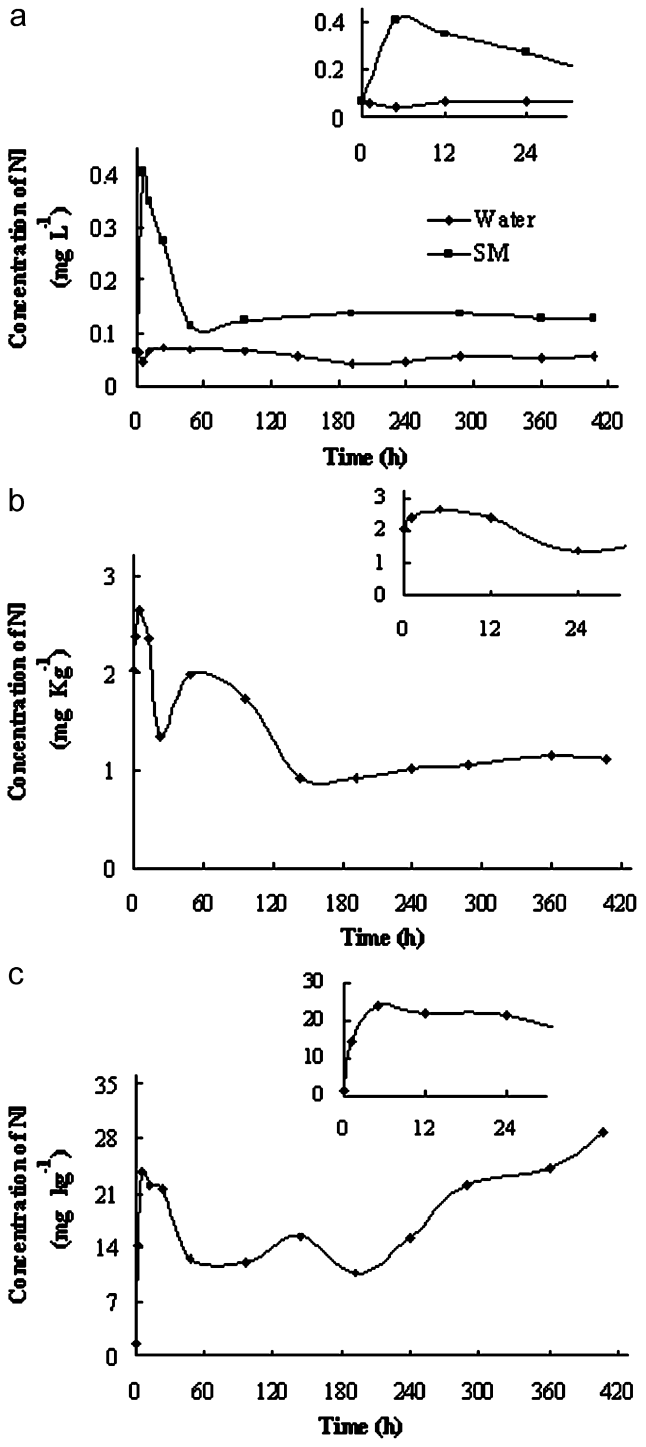

Fig. 2 – NP concentration in water/SM (a), sediment (b) and biota (c), as a function of time.

combined result of sediment of large granule with short sedimentation period and high water concentration of NP.

3.1.3. *Biota*

Fig. 2(c) shows the concentration of NP in the zebra fish. It can be seen that the concentration of NP in the zebra fish increased steeply from 1.57 mg kg^{-1} at 0 h to 23.7 mg kg^{-1} at 5 h. The concentration of NP in the zebra fish fluctuated in the first 300 h. However, as soon as the self-adapting phase ended, the concentration of NP in the zebra fish increased again. At the end of the experiment (408 h), the concentration of NP in the zebra fish did not reach a steady state but continued to increase. The bioconcentration factor (BCF) reached 540 at 408 h and was increasing. NP concentration in the zebra fish did not reach an equilibrium condition at 408 h, at which the concentration of NP was 28.9 mg kg^{-1}. Alkylphenolic compounds are hydrophobic as well as lipophilic; therefore, they accumulate in the sediment and aquatic biota in natural systems (Ahel et al., 1994a, b). It has been reported that NP accumulation in fish exposed to waterborne NP results in a more even distribution of NP among the internal organs than the accumulation due to intragastric NP exposure (Arukwe et al. 2000a, b). Uguz et al. (2003) reported BCF of NP in the tissues of rainbow trout as 4; Snyder et al. (2001) reported BCF of NP in fathead ninnows (*Pimephales oromelas*) as 245–380. Servos (1999) reviewed that BCFs of NP in different fish species ranged from 0.9 to 741. Comparing our data with those mentioned above, it can be seen that BCFs were different, because the concentrations of NP in water were different and different fish species may have different adaptabilities to experimental conditions. In addition, Ekelund et al. (1990) reported BCFs of 90–110 for shrimp (*crangon*); 2740–4120 for common mussel (*Mytilus edulis*); and

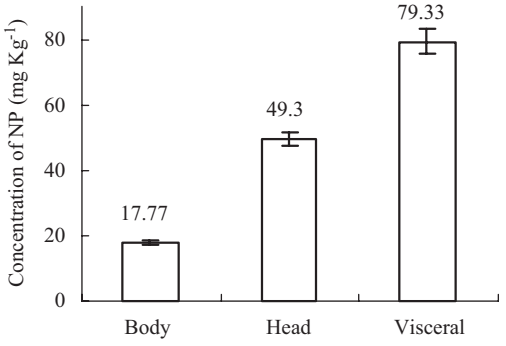

Fig. 3 – NP concentration in different parts of the zebra fish at 408 h.

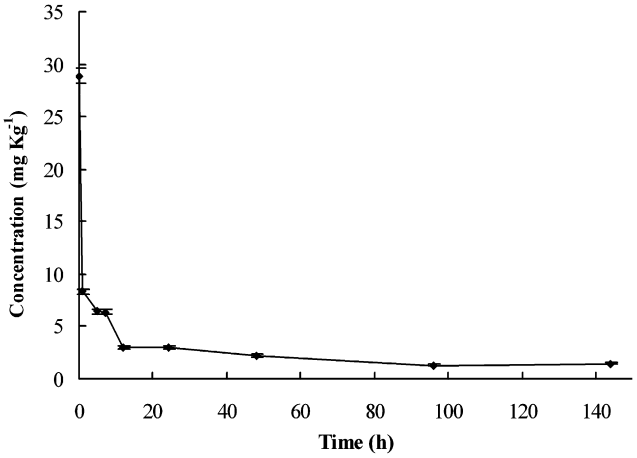

Fig. 4 – NP concentration in the polluted zebra fish as a function of time, when fish was placed in clean water.

1200–1300 for stickleback (*gasterostrus aculeatus*). The above data reported in most literature indicate that BCFs of NP in other biota were higher than that in zebra fish.

Fig. 3 shows the concentrations of NP in different parts of the zebra fish at 408 h. It is apparent that the distribution of NP in the viscera of the zebra fish is the highest (79.33 mg kg^{-1}), corresponding to a BCF of 1440. This is because the viscera have the highest lipid content compared to the body and **head of the zebra fish. Ahel and Giger (1993) also reported that the content of lipid in viscera was much higher than that in muscle, since the log K_{ow} is 4.48. This result is also in agreement with that of other studies (Ekelund et al., 1990; Lewis and Lech, 1996; Arukwe et al., 2000a).

3.1.4. *Depuration of NP in zebra fish*

When the polluted zebra fish were placed into clean water (without NP), the concentration variation of NP in zebra fish with time is shown in Fig. 4. It can be seen that the concentration of NP in zebra fish decreased rapidly from 28.9 mg kg^{-1} at 0 h to 3.03 mg kg^{-1} at 12 h, and then to 1.50 mg kg^{-1} at 144 h (6 days). The depuration half-life of NP in zebra fish was 48 h calculated from the lnC-time analysis for the first-order kinetics. This result showed that the pollutant level of zebra fish decreased dramatically when zebra fish were free from the polluted environment. McLeese et al. (1981) and Ekelund et al. (1993) reported that the clearance of NP in muscle was very rapid. The former also reported a clearance half-life of only 0.3 days of NP in muscle. However, the residual concentration of NP in zebra fish was still relatively high, which showed that the NP could not be depurated completely from zebra fish. This implies that the bioaccumulation of NP through the food chain may pose a significant risk to human health.

3.2. *Fugacity model*

3.2.1. *Fugacity model equations and parameters*

In the microcosm, there were four compartments including SM, water, sediment and biota (zebra fish). The compartment volume, density and *Z* values are given in Table 2.

The rates of transport and transformation processes (mol h^{-1}) are expressed in terms of *D* values (mol Pa^{-1} h^{-1}).

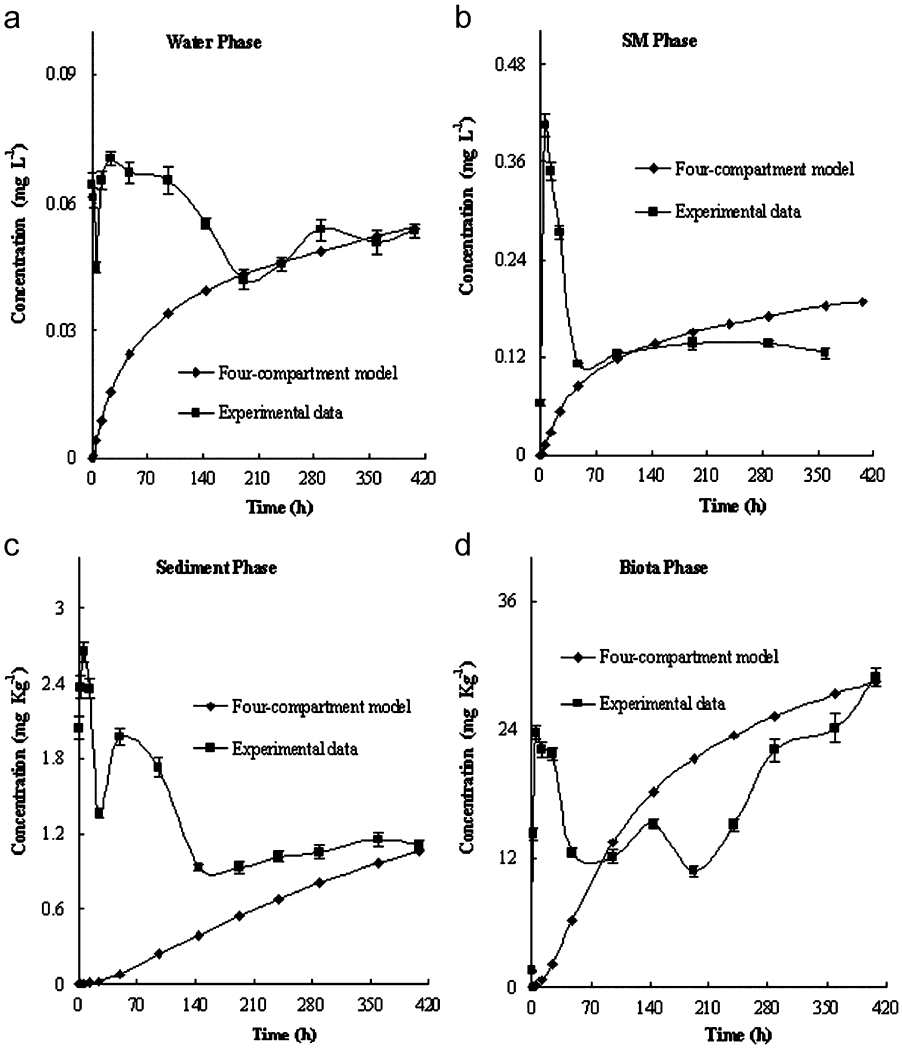

Fig. 5 – (a–d) Measured and calculated concentrations of NP in the microcosm as a function of time. The calculated concentrations of NP were based on a four-compartment model.

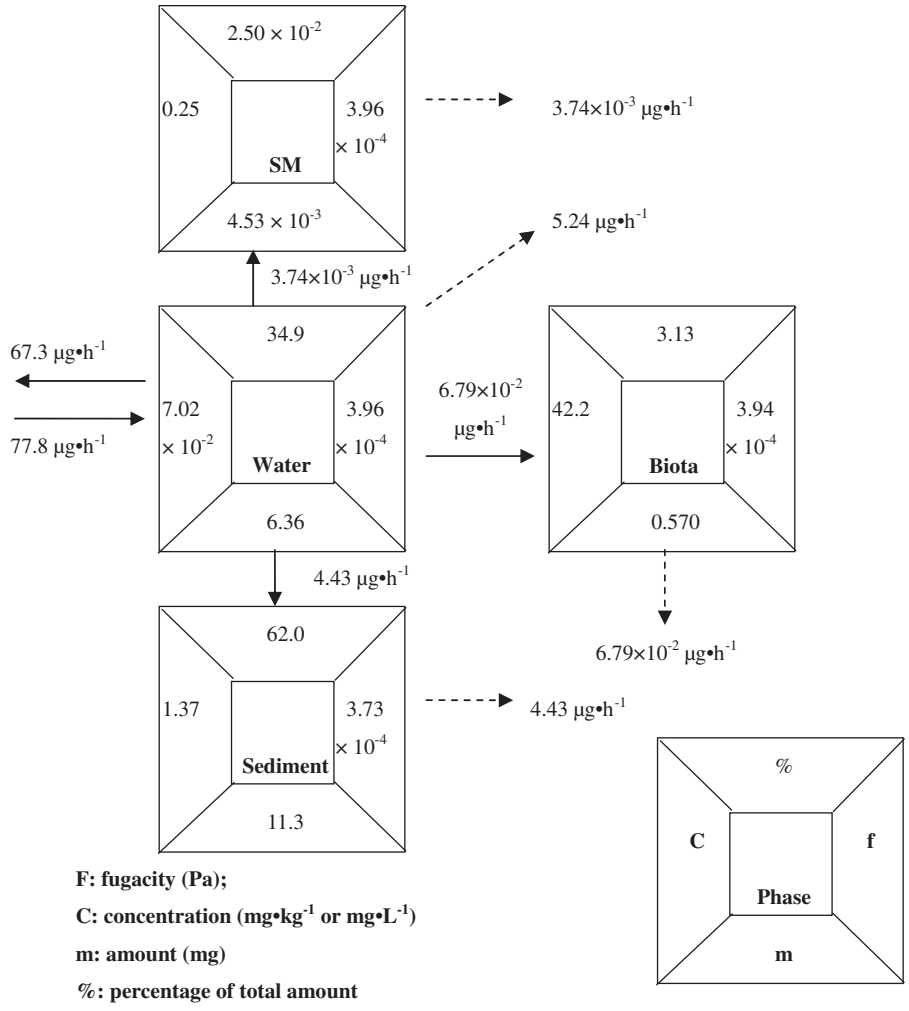

Fig. 6 – Steady-state mass balance of NP in the microcosm.

The processes in the four-compartment system are illustrated in Fig. 1.

Defining fugacity of SM phase, water phase, sediment phase and biota phase as f_M, f_W, f_S and f_B, respectively, unsteady-state mass balance equations for a specific time (t) can be written as follows (Eqs. (2)–(5)):

Water phase:

$$V_W Z_W df_W/dt = E_W + f_S D_{SW} + f_B D_{BW} + f_M D_{MW} - f_W(D_{WS} + D_{WR} + D_{WM} + D_{OUT} + D_{WB}). \quad (2)$$

The SM phase:

$$V_M Z_M df_M/dt = f_W D_{WM} - f_M(D_{MR} + D_{MW}). \quad (3)$$

Sediment phase:

$$V_S Z_S df_S/dt = f_W D_{WS} - f_S(D_{SR} + D_{SW}). \quad (4)$$

Biota phase:

$$V_B Z_B df_B/dt = f_W D_{WB} - f_B(D_{BR} + D_{BW}). \quad (5)$$

The equations are solved by the Runge-Kutta method. The initial input fugacities of SM, water, sediment and biota for the model were all 0 Pa. The inflow rate of NP (i.e. E_W) was 3.53×10^{-7} mol h^{-1}. The other input parameters were given in Tables 2 and 3.

The *D* values for modeling the fate of NP were calculated from expressions (Mackay, 2001) given in Table 3.

3.2.2. *Model application*

As shown in Fig. 5(a–d), the calculation results of the four-compartment model match fairly well with the experimental data, especially towards the end of the experiment. According to the model calculation, when the experiments were completed, the four compartments did not reach a steady state. The results of the fugacity model calculations under unsteady state conditions were in agreement with the data obtained from the experiments.

The mass balance under steady-state conditions is illustrated in Fig. 6. As shown in Fig. 6, 86.50% of all NP input was removed by advective outflow; the remainder was distributed to the 4 compartments as follows: 43.89% into the water phase, 3.13% into the biota phase, 61.99% into the sediment phase and 2.5×10^{-2}% into the SM phase. This finding demonstrates that sediment plays a key role in the fate of NP, acting as a sink of this compound in the aquatic environment.

4. Conclusions

In this study, it was found that NP dispersed rapidly into the four compartments, namely water, SM, sediment and biota (zebra fish), after being delivered into the microcosm. NP could be concentrated onto SM to a concentration of 0.405 mg l^{-1} at 5 h. The concentrations of NP in water and sediment were 0.0535 mg l^{-1} and 1.11 mg kg^{-1}, respectively, at 408 h. The zebra fish accumulated NP rapidly, reaching a concentration of 23.7 mg kg^{-1} at 5 h, then fluctuated in the first 300 h and continued to increase afterwards. At the end of the experiment (408 h), BCF reached 540 and was increasing. The concentration of NP was found to be the highest in the viscera (79.33 mg kg^{-1}), corresponding to a BCF of 1400. NP could be depurated from the zebra fish when the fish was put in fresh water, but the concentration of the residue NP was still high (1.50 mg kg^{-1}), which exhibits an adverse effect on human beings through the food chain.

Results obtained from fugacity model (level III and level IV) calculations were in good agreement with those of the experiments (see Figs. 5(a–d) and 6). This demonstrates that sediment is the key sink of NP in the aquatic environment.

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