Desorption kinetics of naphthalene from sediment particles: batch and stepwise desorption approach

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ABSTRACT

We investigated three major parameters in simulating desorption behaviours: the pre-contamination period, dilution by clean water mass (dilution ratio) and the length of the time interval between dilutions, in both batch and stepwise desorption experiments using particles pre-contaminated with a polycyclic aromatic hydrocarbon, naphthalene (NAPH). We found that the dilution ratio plays a major role in batch desorption, whereas the pre-contamination period plays a major role in stepwise desorption (SD). In addition, the diffusion process was found to be the rate-determining step for our study of SD kinetics. Based on the results of our batch experiments, we were able to derive a mathematical expression capable of correlating the SD rate constant with the length of time interval between dilutions. This expression can be applied in numerical modelling of various naturally occurring processes such as the dispersion and dilution of a heavily contaminated water mass in a marine environment due to an oil spill incident.

Key words | desorption kinetics, dilution ratio, pollutant transport, polycyclic aromatic hydrocarbons, rate constant

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INTRODUCTION

Sorption and desorption processes often affect the transport and fate of hydrophobic organic compounds (HOCs) in surface and subsurface aquatic environments. When dissolved HOCs are sequestered onto other compartments such as soil or sediment, their degradation rates are altered. Moreover, sorption of these contaminants often leads to a change in their mobility, bioavailability and toxicity, and hence leads to a change in the extent of their ecological adverse effects (Luthy *et al.* 1997; Alexander 2000; Sun *et al.* 2003). In general, this sorption process is a hydrophobic interaction and is controlled by the partitioning of pollutants in organic matter (Chiou *et al.* 1979; Karickhoff *et al.* 1979; Means *et al.* 1980). Therefore, sorption capacity is primarily controlled by the hydrophobicity of the sorbate and the organic matter of the sorbent.

The mechanism behind the sequestration of organic contaminants on particles has not been fully understood. It has been proposed that this process mainly involves surface adsorption, entrapment into nanopores and partitioning into the netted area of soil organic matter (Alexander 2000; Ghosh *et al.* 2000; Sun *et al.* 2003). Kinetically, the sorption and desorption of organic contaminants is generally described by a two-stage model: the fast stage, which is measured on a time scale of hours to days, and the slow and very slow stage, which is measured over months to years (Brusseau *et al.* 1991; Oen *et al.* 2006; van den Heuvel & van Noort 2006). Several mechanisms may be involved in this process. Karickhoff & Morris (1985) proposed that particles have labile and nonlabile compartments. The labile compartment is for fast sorption or desorption, while the nonlabile compartment is for slow sorption or desorption. Two-stage sorption or desorption can be explained, according to Xing *et al.* (1996) and Xing & Pignatello (1997), by a dual-mode model in which the rubbery and glassy polymer domains are differentiated in the sorbent. Usually the diffusing rate of organic

contaminants into the domain of a glassy polymer is much smaller than that of a rubbery polymer. Therefore, it would stand to reason that the hole-filling and diffusion of organic contaminants into glassy polymers are more important for slow sorption or desorption. Moreover, Jonker et al. (2005) mentioned that the desorption of coal and combustion-derived PAHs from soot materials can be even slower than the 'very slow' desorption usually observed in sediments. Ahmed & Chen (2006) claimed that aged contaminated material spent longer time desorbing than freshly contaminated material. Cornelissen et al. (1997) suggested a first-order two-compartment model of sorption and desorption processes:

$$\frac{S(t)}{S_e} = F_1 \cdot \exp(-k_1 \cdot t) + F_2 \cdot \exp(-k_2 \cdot t) \quad (1)$$

where $S(t)$ and S_e denote the sorption capacity of contaminants on particles at time t and at equilibrium, respectively; F_1 and F_2 denote the fraction of fast and slow sorption or desorption sites (%), respectively; k_1 and k_2 denote the rate constants of fast and slow sorption or desorption (h^{-1}), respectively. Moreover, Pignatello & Xing (1996) suggested that the fraction of slow compartment increases with contact time caused by the slow penetration of contaminants into more remote parts of the sediment.

The objective of the present study is to understand how three important factors, the length of the pre-contamination period, dilution by clean water mass (dilution ratio) and the length of time interval between dilutions, influence the desorption behaviours of naphthalene by using batch and stepwise approaches.

MATERIALS AND METHODS

Chemicals

Naphthalene (NAPH) (purity, 98%; Tokyo Kasei Organic Chemicals Co.) was chosen as the target contaminant in this study and was used directly without further purification. The stock solution of NAPH was dissolved in methanol (HPLC grade, Mallinckodt, USA). The aqueous NAPH solution for pre-contamination sorption experiments was diluted with 0.5% (w/v) sodium azide aqueous solution to suppress biological activity. The methanol fractions in these

aqueous solutions were all less than 0.1%, rendering its co-solvent effects negligible (Schlautman & Morgan 1993). The water used in all experiments was processed by a Milli-RO^{plus}/Milli-Q water purification device.

Preparation of pre-contaminated sediment particles

The sediment particles used in this study were sediment collected from the Kaoping River in southern Taiwan. A portion of screened (1 mm) sediment slurry was analysed for particle size with Coulter LS particle size analyser (Fang et al. 2007). This subsample (about 0.2 g) was repeatedly acidified with 2 N HCl and washed with Milli-Q water in sequence three times in a ceramic crucible. It was then dried in an oven at 60°C and analysed for organic carbon (OC) using an LECO CS-244 analyser. The particle size range and organic carbon content of the sediment were 16.7–182 μm and 1.28%, respectively. To prepare the pre-contaminated sediment particles, 35 mL aqueous NAPH solution (1 mg L^{-1}) was added into a series of 40 mL amber tubes, each containing 10 g (dry weight) of sediment particles. The tubes were capped and placed on the revolving apparatus in the dark for three sorption periods of 1, 6, and 15 days, after which the respective tubes were centrifuged at 2,000 rpm for 10 min to separate the solution from the solid phase. We then measured PAHs concentration in supernatant solution, which was defined as C_e' in later discussions.

Batch desorption kinetics experiments

After the pre-contamination process of the studied sediment particles, the resulting solutions were then diluted by clean water to cause the contaminants to desorb from the particles. Briefly, the supernatant solution from each tube was replaced with the same volume of water. The dilution ratio is defined as the ratio of the total volume of the original solution and the volume of the residual solution left before adding water. Then, the tubes were placed on a revolving apparatus in the dark. At different specified times, the individual tubes were removed from the apparatus and centrifuged at 2,000 rpm for 10 min. We then measured the NAPH concentration in the supernatant solution, which was defined as $C(t)$ in later discussions.

Stepwise desorption kinetics experiments

For stepwise desorption (SD) experiments, each tube was centrifuged at 2,000 rpm for 10 min to separate solution and solid phase after pre-contamination. Then, a specified volume of the supernatant solution was replaced with the same volume of water and shaken by hand for mixing. The tube was then centrifuged once more at 2,000 rpm for 10 min. We then measured the NAPH concentration in the supernatant solution. The procedures were repeated at specific lengths of time intervals, $\Delta t'$, defined as the time interval in between dilutions for several times.

Analytical procedure

The NAPH concentration was determined by a HPLC-fluorescence detector system. The system includes a Shimadzu LC-pump (LC-9A), a reverse-phase LC-column (LiChroCART® 125-4 RP-18 (5 μm)) and a fluorescence detector (Shimadzu RF-551). The compounds were separated using an isocratic elution with 35% H_2O and 65% acetonitrile. All analyses were performed at a flow rate of 1.5 mL min^{-1} with an injection volume of 20 μL. The excitation and emission wavelengths of NAPH were 276 nm and 366 nm, respectively.

RESULTS AND DISCUSSION

Batch desorption kinetics

The influence of the length of the pre-contamination period

The desorption kinetics of NAPH from sediment particles are shown in Figures 1–3. For the short pre-contamination periods, especially 1 day, NAPH desorbed from the solid phase initially and then some of the released NAPH sorbed back on the particles as time elapsed (Figure 1). The initial desorption was driven by the concentration gradient soon after dilution. The maximum desorption capacity, $C(t)/C_e$, which C_e is the equilibrium concentration in the supernatant solution, peaked at about 5–6 h, after which the sorption of NAPH was driven by the LeChâtelier's principle until equilibrium was reached, which can be explained further by the two-box model.
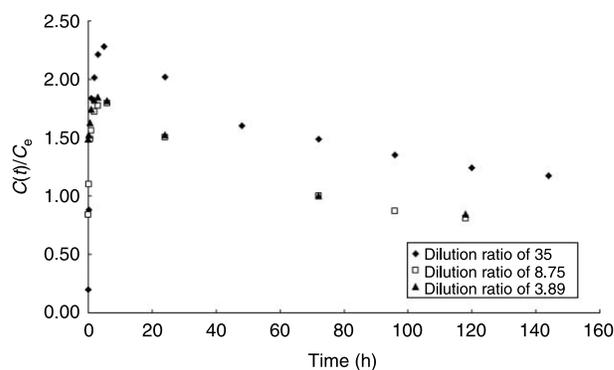

Figure 1 │ The desorption kinetics of naphthalene from pre-contaminated sediments with different dilution ratios with one day for pre-contamination period.

For shorter pre-contamination periods, there was not enough time for NAPH to sorb on the slow sorption compartments during the pre-contamination step (Figure 4). According to the first-order two-compartment model (Cornelissen *et al.* 1997), the fraction of contaminants present in fast and slow compartments could be deduced to be 76.6% and 23.4% (Figure 4), respectively. When NAPH-free water was added, an initial desorption from the fast compartment increased the NAPH desorption capacity. After the maximum desorption capacity was reached, a sorption process followed to fill-up the vacancy in the slow sorption compartment, decreasing the NAPH desorption capacity. For the longest sorption period, 15 days, only desorption was observed (Figure 2). The missing follow-up sorption process provides evidence that the equilibrium was reached substantially in the slow compartment during the pre-contamination step.
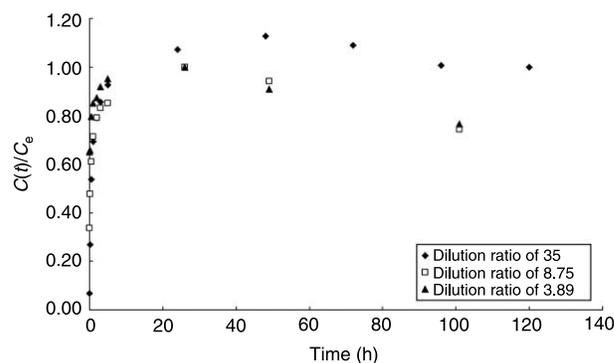

Figure 2 │ The desorption kinetics of naphthalene from pre-contaminated sediments with different dilution ratios with 6 days for pre-contamination period.
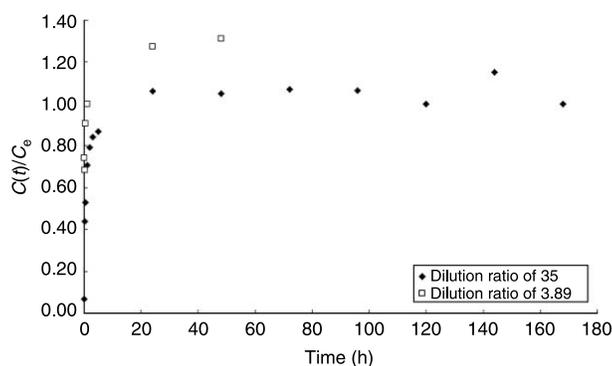
Figure 3 | The desorption kinetics of naphthalene from pre-contaminated sediments with different dilution ratios with 15 days for pre-contamination period.

The influence of dilution ratio

To understand how desorption rate was influenced by the magnitude of change in contaminant concentration change resulting from dilution, two other dilution ratios, 8.75 and 3.89, were studied. The desorption kinetics curves of dilution ratio 8.75 and 3.89 had a similar shape as that for 35 (Figures 1–3).

For the desorption process of the initial 5 h in all cases, the desorption quotient, $C(t)/C'_e$, did not vary much in relationship to the length of the sorption period (paired *t*-test, $p > 0.05$), where $C(t)$ and C'_e represent NAPH concentration in solution at time t, and the NAPH concentration in the solution after the pre-contamination process, respectively. Contrarily, significant difference in the desorption quotient was found among three dilution ratios (paired *t*-test, $p < 0.05$, Figure 5). Therefore, the magnitude of the concentration gradient was found to influence the initial desorption process more than the pre-contamination
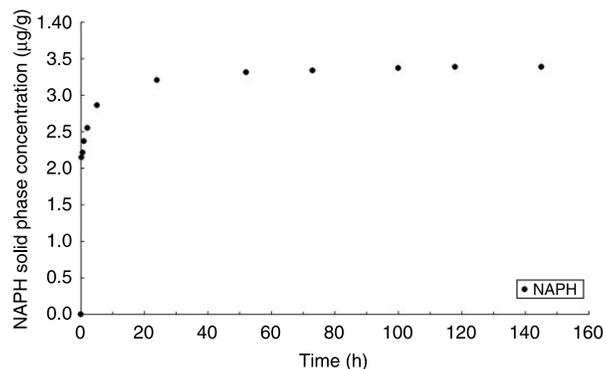

Figure 4 | The sorption kinetics of naphthalene on the studied sediment (1 mg L^{-1}, 3.5 mL g^{-1} sediment).
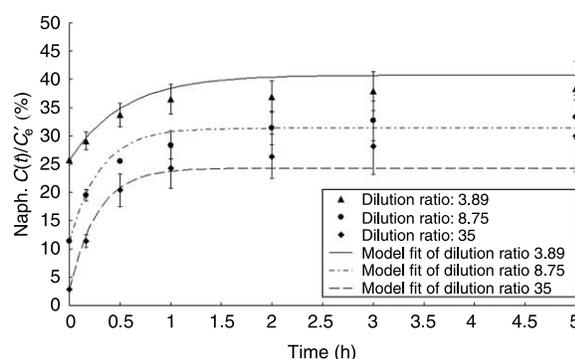

Figure 5 | Desorption kinetics of naphthalene in batch desorption experiments (pre-contamination period: 6 days).

period. Moreover, the relationship between $C(t)$ and C'_e could be expressed as

$$C(t) = B \cdot C'_e + (A - B) \cdot C'_e \cdot \exp(-k_{-1} \times t) \qquad (2)$$

where A represents the ratio of the concentration of contaminant in solution at the initial stage of desorption immediately after dilution to C'_e (i.e. $C(0)/C'_e$), B is the ratio of the concentration of contaminant in solution at the end of desorption experiment (t_{end}) to C'_e (i.e. $C(t_{end})/C'_e$), and k_{-1} is the initial desorption rate constant (h^{-1}). Using this equation, the initial desorption parameters for NAPH could be calculated under different dilution ratios (Table 1). A and B increased as the dilution ratio decreased, whereas the initial desorption rate constants, k_{-1}, increased as the dilution ratio increased. This demonstrates the importance of dilution ratio to the initial desorption rate in our batch experiments.

Stepwise desorption kinetics

The influence of the length of the pre-contamination period

A series of stepwise desorption (SD) experiments were performed. Initially, the length of time interval between

Table 1 | The kinetic parameters (Equation (2)) of batch desorption experiments of NAPH with different dilution ratio

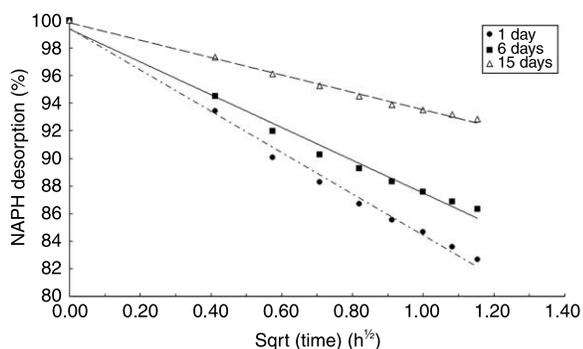| Dilution ratio	35	8.75	3.89
A	0.0286	0.1143	0.2571
B	0.2433	0.3138	0.4075
$(A-B)$	−0.2147	−0.1995	−0.1504
k_{-1} (h^{-1})	3.62	3.32	1.86

Figure 6 | Relationship between normalised naphthalene solid phase concentration and square root of desorption time (pre-contamination period: 1 day; dilution ratio: 35; time interval of dilution: 10 min).

dilutions was set at 10 min. There seemed to be a linear relationship between the normalised NAPH solid phase concentration, $(Q(t)/Q_e)$, and the square root of the desorption time (t) (Figure 6). This could be expressed as:

$$\frac{Q(t)}{Q_e} = -k' \times \sqrt{t} + 1 \qquad (3)$$

where $Q(t)$ represented the NAPH solid phase concentration at desorption time t ($\mu g\, g^{-1}$), Q_e is the NAPH solid phase concentration before desorption ($\mu g\, g^{-1}$), and k' ($h^{-0.5}$) is the rate constant of stepwise desorption. Expressed this way, the rate-determination step used to characterise the SD kinetics should be the diffusion process (Kookana *et al.* 1992). Besides, Oen *et al.* (2006) proposed that intraparticle diffusion process often plays an important role in desorption behaviour. Using this expression, the slope seen in Figure 6 represents the SD rate constant, k' (Table 2). Using the same dilution ratio, the longer the pre-contamination period, the slower is the desorption rate, a result of the increased amount of NAPH sorbed on slow sorption compartment. In addition, significant differ-

Table 2 | The rate constant, k' ($h^{-0.5}$), of SD experiments with different length of sorption period and dilution ratio

Sorption period/ dilution ratio	35	(R^2)	8.75	(R^2)	3.89	(R^2)
1 day	15.0	0.993	15.0	0.993	13.5	0.987
6 days	11.9	0.988	10.1	0.997	9.67	0.989
15 days	6.30	0.996	5.91	0.996	6.02	0.964

ence in rate constants was observed among three pre-contamination periods (paired *t*-test, $p < 0.05$). It should be addressed here that the SD process can be used to simulate naturally occurring processes in the field. For example, in an oil pollution case, particulates can be immersed in a polluted water mass for several days and then the water mass can become cleaner and cleaner as the polluted water mass disperses into the surrounding aquatic environment. This process can be pictured as changing with clean water several times. The longer the immersing time, the smaller is the desorption rate.

The influence of dilution ratio

As observed in the batch desorption experiment, the dilution ratio achieved by changing clean water may also influence the concentration gradient of contaminant in bulk solution. To confirm this, two other dilution ratios, 8.75 and 3.89, in SD experiments were also executed in addition to the dilution ratio of 35 (Figure 6). These two sets of experiments also resulted in the same rate expression and the SD rate constants in sample with different length of pre-contamination periods and different dilution ratios (Table 2). Compared to the batch experiment, although the SD experiment found that desorption rate constant slightly increased along with an increase in the dilution ratio, no significant difference in rate constants existed among three dilution ratios (paired *t*-test, $p > 0.05$). Unlike the finding of the batch experiment, the pre-contamination period was therefore more influential than the dilution ratio in controlling the desorption rate constant in the SD experiment (Table 2).

The influence of the length of time intervals between dilutions

Based on the results presented thus far, both the dilution ratio and the pre-contamination period significantly influence contaminant desorption behaviour in both batch and stepwise desorption experiments. The effect of the length of time interval between dilutions in SD experiments has not been discussed. We used the batch desorption experiment results to estimate the contaminant concentration variation in the solution phase after each dilution

at a specific length of the dilution time interval, $\Delta t'$. If we set t' to equal to $\Delta t'$ in Equation (2), then:

$$C(\Delta t') = B \cdot C_e' + (A - B) \cdot C_e' \cdot \exp(-k_{-1} \cdot \Delta t') \qquad (4)$$

By doing this, we were able to obtain the variation of solid phase concentration after a specific length of time interval, $\Delta t'$:

$$Q_e - Q(\Delta t') = (B - A) \cdot C_e' \cdot [1 - \exp(-k_{-1} \times \Delta t')] \cdot \frac{V}{W} \qquad (5)$$

In the above equation, V represents the volume of solution in batch experiment (L), and W is the weight of particles in batch experiment (g). Finally, after combining Equation (5) into Equation (3), the SD rate constant, k', could be written as the following equation.

$$
\begin{aligned}
k' &= \frac{Q_e - Q(\Delta t')}{Q_e \cdot \sqrt{\Delta t'}} \\
&= \frac{(B - A) \cdot C_e' \cdot [1 - \exp(-k_{-1} \times \Delta t')] \cdot \frac{V}{W}}{Q_e \cdot \sqrt{\Delta t'}}
\end{aligned} \qquad (6)
$$

The SD rate constant, k', increased initially with the length of time interval of changing clean water, and decreased after reaching a maximum value (Figure 7). To obtain the time interval of k' maximum, $\Delta t'_{max}$, we could take differential on k' and make it equal to zero:

$$\frac{dk'}{d(\Delta t')} = 0$$

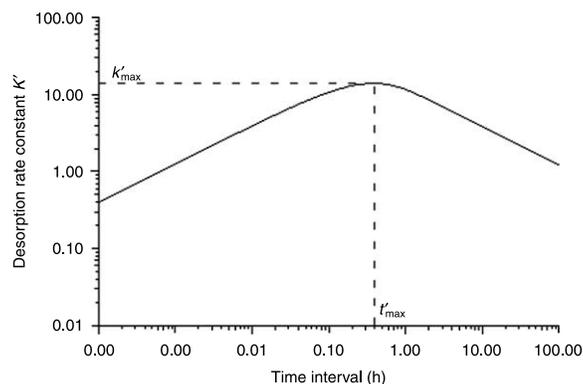$$\exp(k_{-1} \cdot \Delta t') = \frac{1}{2 \cdot k_{-1} \times \Delta t' + 1}$$

Figure 7 | Relationship between the stepwise dilution desorption rate constant, k', and the length of time interval of changing clean water, $\Delta t'$.

Table 3 | Comparison of the experimental and model (Equation (6)) predicted k' values ($h^{-0.5}$) of different dilution time interval

Dilution time interval	12 min	24 min	60 min
Experimental k' value	11.5	12.9	10.7
Model predicted k' value	11.3	12.8	9.08

This results in $k_{-1} \times \Delta t'$ equalling 1.256 for maximum k'. We could then estimate $\Delta t'_{max}$ by using the values of k_{-1} from different batch experiments. For a very large $\Delta t'$, the SD processes behaved like near-equilibrium batch processes in series. As $\Delta t'$ decreased, the SD rate constant, k', increased because of the larger concentration gradient resulting from changing water over a shorter time interval. However, as the $\Delta t'$ decreased to a value smaller than the critical $\Delta t'$, $\Delta t'_{max}$, the transport of the sorbate, NAPH, from the slow to the fast compartment became the rate-determination step. Therefore, further decrease of $\Delta t'$ caused the depletion of sorbate in the fast compartment and caused the decrease of the SD rate constant. In other words, $\Delta t'_{max}$ can be viewed as the optimised length of time interval that should be changed to produce the highest stepwise desorption rate. At this optimised length of time interval, the rate of desorption from the fast compartment is equal to the rate of transportation of the sorbate from the slow to the fast compartment.

In order to confirm the above model (Equation (6)), SD experiments with three different time intervals, 12, 24, and 60 min, were performed while keeping the pre-contamination period and the dilution ratio constant. Our results were comparable to findings predicted by the model (Table 3). Our maximum was confirmed. We could then use the results of the batch experiments, which are easier to conduct than SD experiments, in different conditions to deduce the stepwise desorption rate expressions for changing the surrounding contaminant concentrations. This approach can save the considerable amount of time and labour needed to obtain parameters for the numerical simulation of pollutant transport in aquatic environment.

CONCLUSIONS

Several conclusions could be made from this study. First, the results of batch desorption experiments showed that

NAPH desorbs from solid phase initially and then sorbs back to solid phase again until equilibrium is achieved, if the length of the pre-contamination period is not long enough. The dilution ratio of the water was also varied and was found to be the major factor in the batch desorption process. As the dilution ratio increased, the initial rate constant also increased as a result of a higher NAPH concentration gradient. Contrary to the batch desorption experiments, the length of pre-contamination period was found to play a major role in the stepwise desorption process. Finally, we deduced a relationship between the rate constant and the length of time interval of changing clean water from the results of both batch and stepwise desorption experiments. This rate expression depicts an increase of rate constants initially and a decreasing trend after reaching its maximum value with the time interval of changing clean water. This suggests that the time interval is another important factor in the desorption process.

ACKNOWLEDGEMENTS

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