

# Sediment–Porewater Partition of Nonylphenol Polyethoxylates: Field Measurements from Lanzhou Reach of Yellow River, China

Yong Yu · Jian Xu · Hongwen Sun ·  
Shugui Dai

Received: 6 August 2007 / Accepted: 20 December 2007 / Published online: 23 January 2008  
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**Abstract** Nonylphenol polyethoxylates (NPnEO) and nonylphenol (NP) have drawn much environmental concern because of their weak estrogenic activities. The present study focused on the spatial distribution of NPnEO and NP in surface sediments and their corresponding porewaters along Lanzhou Reach of Yellow River, China. Long EO chain NPnEO analogs with  $n > 2$  were not measurable in most sediment and porewater samples, so only NP, nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) were discussed in this study. Concentrations of NP, NP1EO, and NP2EO in the sediments ranged from 61.3 to 113.9, 31.1 to 55.9, and 47.9 to 74.1 ng/g dry weight, respectively. A significant correlation ( $R^2 = 0.56$ ,  $p < 0.01$ ) was observed between NP levels and organic carbon content of the sediments, whereas no correlation was found for the more hydrophilic NP1EO and NP2EO. The concentrations of NP, NP1EO, and NP2EO in the porewaters ranged from 0.35 to 1.95, 0.06 to 0.63, and 0.08 to 0.38  $\mu\text{g/L}$ . The mean *in situ* log  $K_{oc}$  values ( $n = 13$ , S1 excluded) of NP, NP1EO, and NP2EO were 4.48, 4.94, and 5.06, respectively, which were lower than those measured in batch adsorption experiments.

The Yellow River, which is called the Mother River of China, is one of the largest rivers and is named for its highest sand content in the world. It flows across nine

provinces, with a main stream of 5464 km long, and average sand content of  $2.83 \text{ kg/m}^3$ . It is a very important water resource for industry, agriculture, and people's living in the north of China. Lanzhou Reach belongs to the upper reaches of the Yellow River. Large amounts of wastewaters discharge from industries of Lanzhou City, making the river in this reach severely polluted. According to our previous investigations, (NPnEOs) is one class of major pollutants in this reach (Xu et al. 2006).

Nonylphenol polyethoxylates are one of the most widely used nonionic surfactants, which have been used as industrial and domestic detergents, pesticides, emulsifier formulations and other industrial products (Ahel et al. 1994). Approximately 700 thousand tons of NPnEO are produced annually worldwide (Jonkers et al. 2005), with 50 thousand tons in China. About 60% of the surfactant finally enters natural water environments via various pathways, such as municipal or industrial wastewater discharges and sewage treatment plant (STP) effluents (Ying et al. 2002).

Once NPnEOs are present in water bodies, they are degraded into relative stable small metabolites, such as nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), and nonylphenol diethoxylate (NP2EO) (La et al. 2001). Unfortunately, many studies (Berryman et al. 2004; Shang et al. 1999) have reported that the small NPnEO metabolites are more toxic and persistent than their parent substances. Moreover, weak estrogenicity to fish, bird, and mammal cells *in vitro* was also observed (Jobling and Sumpter 1993; Ying et al. 2002).

In China, NPnEO and NP contamination has been found in many aquatic environments. For example, Chen et al. (2006) reported that NP concentrations ranged from 59 to 7808 ng/g in sediments and from 0.02 to 0.628  $\mu\text{g/L}$  in water samples of the Pear River Delta. Hu et al. (2005) found that the concentrations of NPnEO in sediments of the South

Y. Yu · J. Xu · H. Sun (✉) · S. Dai  
Key Laboratory of Environmental Pollution Process and  
Standard of Ministry of Education, College of Environmental  
Science and Engineering, Nankai University, Tianjin 300071,  
People's Republic of China  
e-mail: sunhongwen@nankai.edu.cn

Sewage River, Tianjin, China ranged from 143 to 9700 ng/g wet weight and NP sediments ranged from 17.8 to 970 ng/g. Shao et al. (2005) reported that NP concentrations ranged from 0.02 to 6.85  $\mu\text{g/L}$  in the water column of the Yangtze River and the Jialing River at Chongqing Valley.

In order to assess the fate of small NPnEO metabolites in aquatic environments, their partition behavior should be well understood. Sediment–porewater partition is an important process that controls the transport, fate, bio-availability, and ecotoxicological risk of a microlevel of lipophilic contaminants in aquatic environments. However, few studies on the sediment–porewater partition of NPnEO and NP have been reported. Heinis et al. (1999) reported a mean NP porewater concentration of 18.6  $\mu\text{g/L}$  for the period 2–34 days at a 300- $\mu\text{g/L}$  initial concentration in a NP persistence study. However, they focused on the distribution of NP in porewater and its sediment–porewater partition was still scarce. The objective of the present study was to investigate the distribution of NP and NPnEO in sediments and their sediment–porewater partition in the Lanzhou Reach of the Yellow River in China.

## Materials and Methods

### Chemicals and Instrumentation

Standards of NP, NP1EO, and NP2EO (technical grade) were purchased from Tokyo Chemical Synthesis (Tokyo, Japan). NPnEO ( $n = 1–15$ , standard) was from Hayashi Pure Chemical (Osaka, Japan). Isopropanol and *n*-hexane, used as the mobile phase of high-performance liquid chromatography (HPLC) analysis, were of HPLC grade, and dichloromethane (DCM), ethyl ether, and anhydrous sodium sulfate were of analytical grade. Ultrapure water was obtained using a Millipore Ultra-pure Water System (USA). Florisil (60–100  $\mu\text{m}$  mesh size; Tianjin Chemical Reagent Corp., China) was activated at 130°C for 16 h before use.

A Waters 1525 HPLC with a Waters 2475 fluorescence detector (Waters Company, USA) was utilized for chemical analysis in this study. A Waters W2108N007  $\text{NH}_2$  column ( $\mu\text{Bondapak}$  3.9 mm inner diameter  $\times$  300 mm  $\times$  10  $\mu\text{m}$ ; Waters Corp., Ireland) was used for separation of NPnEO analogues.

### Sampling and Sample Treatment

Fourteen surface sediment samples were collected along the river in Lanzhou Reach on July, 20, 2005. Sampling locations are shown in Figure 1. The surface sediment samples (0–20 cm) were collected using a stainless-steel grab sampler at the center of the river. The samples were

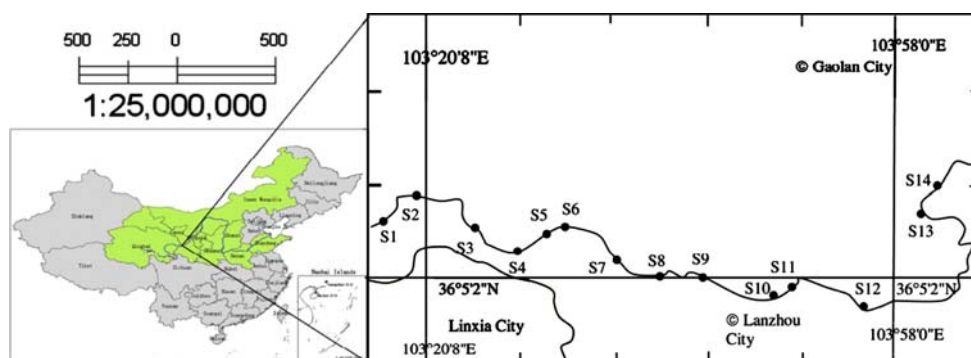
placed in glass bottles with Teflon-lined caps and transported to the laboratory promptly, where they were stored at  $-20^\circ\text{C}$  until further analysis.

The sediment samples were centrifuged in 250-mL glass centrifuge tubes at 4000 rpm for 15 min to separate porewater from the sediment. Five hundred milliliters of isolated porewater and surface water samples were liquid–liquid extracted with  $3 \times 30$  mL DCM, and then the three extracts were combined. A freeze-drier (ALPHR 1–2 LD; Martin Christ Gefriertrocknungsanlagen GmbH, Germany) was used for drying the sediment. Five grams of freeze-dried sediment sample was Soxhlet-extracted with 100 mL DCM at 55°C for 24 h. The obtained extracts were concentrated to about 1 mL at 0.08 MPa, 40–42°C in a water bath by a rotary evaporator (RE-52AA; Shanghai Ya-Rong Biochemical Instrument Factory, China) and then purified by passing through a 25  $\times$  1.0-cm-inner diameter glass clean-up column containing 5 g of hexane-rinsed Florisil and 1 g of anhydrous sodium sulfate. The column was washed with 50 mL hexane and eluted with 80 mL of ethyl ether and hexane (1:9, v/v) for NP, NP1EO, and NP2EO. The elute was concentrated to almost dryness under a gentle  $\text{N}_2$  stream, and 0.5 mL of *n*-hexane was then added to redissolve the residue. The solution was analyzed by HPLC (Xu et al. 2006).

The organic carbon (OC) content of the sediments was determined by the potassium dichromate–sulfuric acid oxidation method. The dissolved organic carbon (DOC) concentrations of porewater and surface water were determined by a high-temperature combustion method (Fukushima et al. 1996).

### Batch Sorption Experiment

The sediment at S10 (Fig. 1) was used to conduct sorption experiment in the laboratory as representing sediment in the Lanzhou Reach due to its relative high OC. The batch experimental procedure for sorption isotherm was detailed in the literature (Hou et al. 2006), and only a brief description is given here. A certain amount of stock solution of NP, NP1EO, and NP2EO was added in 22-mL glass tubes with Teflon-lined caps (VAAP-324020-2385; Shanghai Anpel Instrument Corp., China) to make their initial aqueous concentrations of 0, 50, 100, 200, 500, and 1000  $\mu\text{g/L}$ , respectively. The tubes were filled with 20 mL distilled water containing 0.002 g  $\text{NaN}_3$  after the solvent volatilized and then 0.020 g sediment was added. The tubes were shaken for 12 h at 135 rpm in the dark at  $25 \pm 1^\circ\text{C}$ . Aqueous equilibrium concentrations were measured after the separation of aqueous and solid phases and concentration by liquid–liquid extraction, and solid-phase concentrations were

**Fig. 1** Map of studied area and sampling sites

calculated by mass balance. Each experiment was conducted in duplicate.  $K_d$  values were acquired from the equation of the sorption isotherms, and the OC normalized distribution coefficients ( $K_{oc}$ ) could be calculated according to the definition,  $K_{oc} = K_d/f_{oc}$  ( $f_{oc}$  is the OC content of the sediment).

#### NPnEO Analysis

Mixtures of *n*-hexane/isopropanol (98/2, v/v), and isopropanol/water (98/2, v/v), named solvents A and B, respectively, were used as the mobile phase for HPLC analysis. Gradient elution was carried out with a linear program from 95% A and 5% B to 80% A and 20% B in 10 min with a flow rate of 1.0 mL/min. Excitation and emission wavelengths of the fluorescence detector were 233 and 302 nm, respectively. The injection volume was 20  $\mu$ L (Hou et al. 2006).

#### Quality Assurance and Quality Control

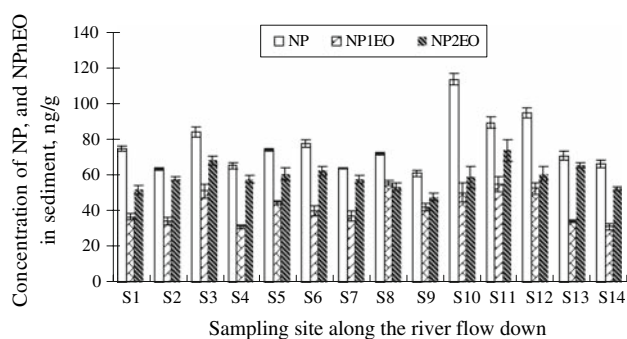
Procedural blanks were analyzed concurrently with the porewater and sediment samples. The porewater blank consisting of 100 mL double-distilled water was extracted in the same manner as the porewater samples. The sediment blank was solvent-extracted sediment that had been baked in a muffle furnace at 450°C overnight and was extracted in the same manner as the sediment samples. The NPnEO concentrations in the sediment and porewater blanks were lower than detection limits of the method, which were 5 ng/g for sediment and 0.01  $\mu$ g/L for porewater. Sediment and porewater samples were spiked with a specific amount of NP, NP1EO, and NP2EO to determine the recovery. The average recoveries and the relative standard deviation (RSD) in sediment and porewater were determined to be  $93 \pm 4\%$  and  $87 \pm 5.1\%$  (NP),  $92 \pm 4\%$  and  $97 \pm 7\%$  (NP1EO), and  $91 \pm 5\%$  and  $96 \pm 6\%$  (NP2EO), respectively. Procedural blanks for batch sorption experiment without sediment indicated that NP,

NP1EO, and NP2EO sorbed on the wall of glass tubes was negligibly small (<3%).

## Results and Discussion

#### NP, NP1EO, and NP2EO Concentrations in Sediment and Porewater Samples

Fourteen sediment samples were collected in Lanzhou Reach, Yellow River, as indicated in Figure 1. Long EO chain NPnEO analogues with  $n > 2$  were below the detection limit in most of the samples, so that only NP, NP1EO, and NP2EO are discussed in this study. NP, NP1EO, and NP2EO concentration in the sediments ranged from 61.3 to 113.9, from 31.1 to 55.9, and from 47.9 to 74.1 ng/g dry weight, with mean values of 76.7, 42.6, and 59.4 ng/g dry weight, respectively (Fig. 2). In all sediment samples, the NP concentration was the highest, followed by NP2EO and NP1EO in a descending order at most sampling sites. Compared with other places in the world, as shown in Table 1, the Lanzhou Reach of the Yellow River was moderately polluted by NP, NP1EO, and NP2EO.



**Fig. 2** Concentrations (ng/g dry weight) of NP, NP1EO, and NP2EO in the sediments at the Lanzhou Reach of the Yellow River. Each value is the mean value  $\pm$  standard deviation of two measurements. NP, NP1EO, and NP2EO levels in sediments were significantly different ( $p < 0.05$ ) between each other except those among S5, S6 and S7 and between S13 and S14

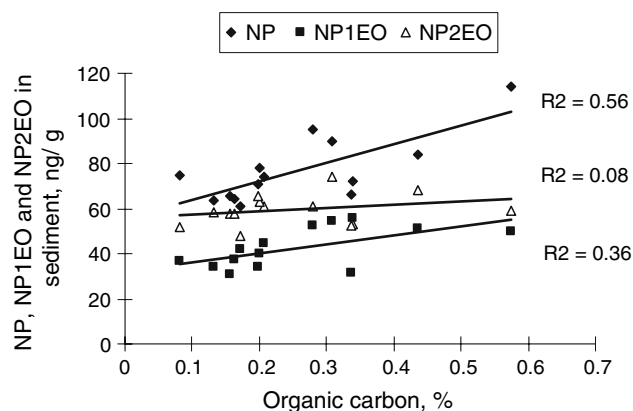
**Table 1** Concentrations (ng/g) of NP, NP1EO, and NP2EO in sediments

| Location                 | NP         | NP1EO     | NP2EO     | Ref.               |
|--------------------------|------------|-----------|-----------|--------------------|
| UK                       | <0.1–1     |           | <0.5–92   | Li et al. (2004)   |
| USA                      | 2.9–2960   | 23–175    |           |                    |
| Canada                   | 0.1–72     | <LOD–38   |           |                    |
| Japan                    | 30–13000   | 10–3470   |           |                    |
| Pear River Delta (China) | 59–7808    |           |           | Chen et al. (2006) |
| Nanpaiwu River (China)   | 17.8–970   |           |           | Hu et al. (2005)   |
| Yellow River (China)     | 61.3–113.9 | 31.1–55.9 | 47.9–74.1 | Present study      |

LOD: limit of detection

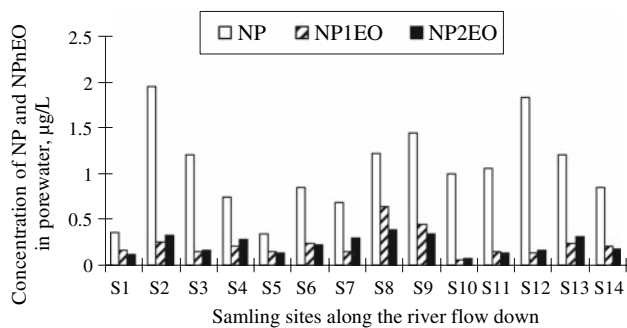
According to Figure 2, the NP concentrations in downstream sediments (S10 to S14) were higher than those in upstream sediments (S1 to S9). An unexpected high concentration of NP was observed in the sediment (with the lowest  $f_{oc}$ ) at S1. S1 was at the start point of the city, and there was no industrial pollution source around. We attribute its heavy NP contamination to the contribution from an upstream branch river, the Huangshui River from Qinghai Province, which was seriously polluted by local discharge. On the other hand, the concentrations of NP1EO and NP2EO at S1 were low. It implies that NP is quite stable in an aquatic environment and could be transported a long way by river flow, whereas NP1EO and NP2EO are relatively easily degraded by biodegradation and photodegradation, and NP is one relatively stable metabolite of their degradation (Wang et al. 2006). Concentrations of the pollutants were high at S10 and S12, which are related to the wastewater discharges from pollution sources along the river. At S12, there is the wastewater discharge pipeline from Lanzhou Chemical Industrial Company, which is the largest discharge pipe in Lanzhou City. S10 is located in the center of the city, and there is a large wastewater discharge stream consisting of municipal and industrial wastewaters. Hence, the high concentrations in the downstream sediments (S10 to S14) might be due to the discharge of effluents containing large amounts of sewage and industrial wastewaters from Lanzhou City. NP, NP1EO, and NP2EO levels in sediments were significantly different ( $p < 0.05$ ) among each other except those among S5, S6, and S7 and between S13 and S14.

The effect of sediment OC on the distribution of NP, NP1EO, and NP2EO was investigated. The OC content ( $f_{oc}$ ) of the sediments in the Lanzhou Reach of the Yellow River ranged from 0.08% to 0.57%. Figure 3 shows the relationship between  $f_{oc}$  and NP, NP1EO, and NP2EO concentrations in the sediments. A moderate correlation for NP was observed ( $R^2 = 0.56$ ,  $p < 0.01$ ), whereas the correlation for NP1EO and NP2EO was poor ( $R^2 = 0.36$ ,  $p < 0.05$  and  $R^2 = 0.08$ ,  $p > 0.05$ , respectively). This indicates that sediment OC plays an important role in controlling NP levels in the sediments (Chen et al. 2006; Xu et al. 2006). The low  $R^2$  for NP1EO and NP2EO was

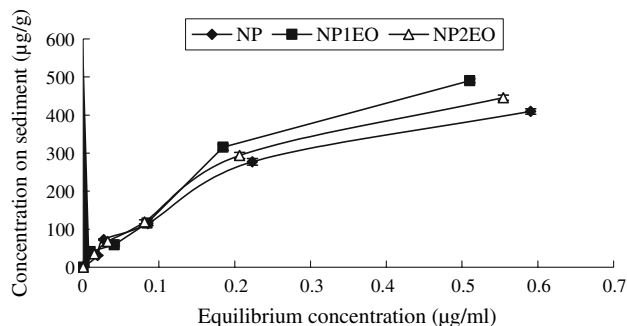
**Fig. 3** Correlation among NP, NP1EO, and NP2EO concentrations and the OC contents in the sediments

consistent with the finding reported by Jin et al. (2004) that NPnEO is more related with inorganic minerals in sediments with the increasing EO chain.

As shown in Figure 4, NP, NP1EO, and NP2EO concentrations in the porewater ranged from 0.35 to 1.95, from 0.06 to 0.63, and from 0.08 to 0.38  $\mu\text{g/L}$ , with mean values of 1.05, 0.23, and 0.22  $\mu\text{g/L}$ , respectively. The NP concentration in the porewaters was greater than for NP1EO and NP2EO. This is because NP is slow in degradation, with a half-life of 2–3 months, compared to NP1EO and NP2EO, whose half-lives are about 3–5 days (Yoshimura 1986; Ying et al. 2002). The two highest concentrations of NP appeared at S2 and S12, where Lanzhou Oil Industrial Company and Lanzhou Chemical Industrial Company, respectively, are located. The wastewater discharges from these two companies account for a large part of the contamination input along this reach. NP, NP1EO, and NP2EO in the surface water of the same sampling sites ranged from 0.065 to 0.672, from 0.08 to 0.451, and from 0.039 to 0.373  $\mu\text{g/L}$ , respectively, which is consistent to the previous investigation by Xu et al. (2006). The NP concentration in surface water and porewater was significantly higher ( $p < 0.05$ ) than NP1EO and NP2EO. The greater input of total NPnEO, together with relative rapid degradation of NP1EO and NP2EO and slow degradation



**Fig. 4** Concentrations (µg/L) of NP, NP1EO, and NP2EO in porewaters at the Lanzhou Reach of the Yellow River



**Fig. 5** Sorption isotherms of NP, NP1EO, and NP2EO on sediment at S10

of NP, led to the accumulation of NP at these sites (Wang et al. 2006; Xu et al. 2006).

**Partitioning Between Sediment and Porewater**

Sorption isotherms of NP, NP1EO, and NP2EO in S10 are shown in Figure 5, and Freundlich isotherm and linear equations were used to describe the data (Table 2). The Freundlich isotherm is based on the assumption that sorption takes place into a heterogeneous medium with a nonlinear equation

$$C_s = K_f \times C_e^{1/n}$$

**Table 2** Sorption isotherm equations of NP, NP1EO, and NP2EO on sediment at S10

|       | Linear                               | Freundlich                                  |
|-------|--------------------------------------|---|
| NP    | $C_s = 776.88C_w,$<br>$R^2 = 0.8158$ | $C_s = 676.08C_w^{0.70},$<br>$R^2 = 0.9471$ |
| NP1EO | $C_s = 1058.1C_w,$<br>$R^2 = 0.8745$ | $C_s = 741.31C_w^{0.68},$<br>$R^2 = 0.9275$ |
| NP2EO | $C_s = 895.02C_w,$<br>$R^2 = 0.8454$ | $C_s = 758.58C_w^{0.71},$<br>$R^2 = 0.9886$ |

where  $C_s$  is the sorbed concentration (µg/g),  $C_e$  is the equilibrium concentration in the solution phase (µg/mL),  $K_f$  is the Freundlich constant showing the capacity of adsorption, and  $1/n$  is a linearity factor that describes the nonlinearity of adsorption. The values of  $K_f$  and  $1/n$  can be obtained from the linear form of the Freundlich isotherm equation

$$\lg C_s = \lg K_f + 1/n \lg C_e.$$

At  $n = 1$ , the equation converts to a linear sorption isotherm:

$$C_s = K_d \times C_e,$$

where  $K_d$  is the distribution coefficient (L/kg).

It can be seen that sorption of NP, NP1EO, and NP2EO in S10 followed the Freundlich isotherm much better than the linear isotherm, and  $\log K_{oc}$  was calculated to be 5.07, 5.11, and 5.12 (Table 3) using  $K_f$  values obtained from Freundlich isotherms.

In order to compare the partition behavior of NPnEO for all the sampling sites, the OC normalized distribution coefficients ( $K'_{oc}$ ) were calculated based on field data:

$$K_d' = C_s/C_{aq},$$

$$K'_{oc} = K_d'/f_{oc},$$

where  $C_s$  is the sediment concentration,  $C_{aq}$  is the concentration in porewater, and  $f_{oc}$  is the sediment fraction of OC.

The mean *in situ*  $\log K'_{oc}$  ( $n = 13$ ) of NP, NP1EO and NP2EO were 4.48, 4.94, and 5.06, respectively (Table 3). The  $\log K'_{oc}$  value at S1 was excluded from calculation because pollution at S1 was more related with the upstream river rather than the Lanzhou Reach. Also included in Table 3 are  $K_{ow}$  values and available  $K_{oc}$  for NP, NP1EO, and NP2EO derived from both laboratory experiments and field investigations reported by others. Ferguson et al. (2001) quantified sorption of NP, NP1EO, and NP2EO on suspended particulate matters (SPMs) in Jamaica Bay with

**Table 3** Partition coefficients for NP, NP1EO, and NP2EO in this study and other lab and field studies

|                | NP   | NP1EO | NP2EO | Ref.                             |
|----------------|------|-------|-------|----------------------------------|
| $\log K_{ow}$  | 4.48 | 4.17  | 4.21  | Ahel et al. (1994)               |
| $\log K_{oc}$  | 5.39 | 5.46  | 5.18  | Ferguson et al. (2001)           |
| ( $n = 5$ )    |      |       |       |                                  |
| $\log K_{oc}$  | 5.60 |       |       | Isobe et al. (2001)              |
| $\log K_{oc}$  | 5.10 |       |       | Van et al. (2000)                |
| $\log K'_{oc}$ | 4.48 | 4.94  | 5.06  | Present study (field)            |
| ( $n = 13$ )   |      |       |       |                                  |
| $\log K_{oc}$  | 5.07 | 5.11  | 5.12  | Present study (batch experiment) |

log  $K_{oc}$  values of 5.39, 5.46, and 5.18, respectively; Isobe et al. (2001) found the log  $K_{oc}$  value of 5.60 for the sorption of NP on aquatic particles.

In the present study, the *in situ* NP log  $K_{oc}'$  value was 0.59 log units lower than the value measured in the batch experiment. We considered possible explanations for this apparent discrepancy between the field study and the sorption experiment. One reason is that the high DOC content in the porewater leads to a lower field  $K_{oc}$ . Porewater is a special phase in the aquatic environment with different aquatic chemical conditions with the above water column. The DOC content in the porewaters of the present study ranged from 16.3 to 23.7 mg/L, significantly higher than those of the surface water, which ranged from 0.7 to 3.2 mg/L. Gschwend and Wu (1985) have found that the high DOC level in the porewater might contribute to the low field  $K_{oc}$ .

Another factor is that the sorbent concentration used in the batch sorption experiment is 1 g/L, which is similar to the sand content of the Yellow River at the Lanzhou Reach. However, the solid–liquid ratio of the *in situ* sediment–porewater system is much higher. Many studies (Donald and John 1980; Schrap et al. 1995; Weber et al. 1983) have reported that sorption at a lower solid–liquid ratio always results in a higher log  $K_{oc}$ .

The third possibility might be that the sorption of NP and degradation of NPnEO in the porewater does not reach equilibrium. NP, with a higher lipophilicity, is expected to reach the adsorption equilibrium slowly (During et al. 2002, Langford et al. 2005). Consequently, NP, generated from the degradation of NPnEO in porewater, might have not reached equilibrium with the sediment, which contributes to the lower concentration of NP in sediment.

The mean *in-situ* log  $K_{oc}'$  ( $n = 13$ ) of NP1EO in the present work was 4.94, 0.17 log units lower than the value measured in the sorption experiment, whereas the mean *in situ* log  $K_{oc}'$  (5.06) of NP2EO was similar to that of the sorption experiment (5.12). Less discrepancy in the batch and field  $K_{oc}$  of NP1EO and NP2EO than that of NP is attributed to NP1EO and NP2EO being less hydrophobic than NP, and the effects from DOC in porewater and nonequilibrium might be less.

## Conclusions

In the present work, the occurrence of NP, NP1EO, and NP2EO in surface sediments and the corresponding porewaters of the Lanzhou Reach of the Yellow River was investigated. The concentration of NP, NP1EO, and NP2EO in the sediments of this reach is at a moderately polluted level compared with those of other places in the world. The sediment–porewater partition of NP, NP1EO,

and NP2EO reveals that their log  $K_{oc}'$  are lower than those measured in the adsorption experiment. We attribute this to the high DOC level in the porewater and nonequilibrium of the field sorption. Further research is required to study the multimedia environmental behavior of NP and NPnEO, which would include sediment, porewater, overlying water, and aquatic organism in order to reveal their fate and support the results by more reliable evidence.

**Acknowledgment** This study was funded by the National Natural Science Foundation of China (No. 20677031, 50239060).

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