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# Distribution and dissipation pathways of nonylphenol polyethoxylates in the Yellow River: Site investigation and lab-scale studies

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## Abstract

Spatial distribution of nonylphenol polyethoxylates (NPEOs) and nonylphenol (NP) was investigated in a field study in Lanzhou Reach of the Yellow River. NPEOs and their metabolites were found in the river, with the maximum dissolved concentrations of 6.38 nmol/L for NPEOs, 0.19 nmol/L for nonylphenol ethoxy acetic acids (NPECs) and 0.79 nmol/L for NP, respectively. The maximum concentrations in the sediment and suspended particle samples were 1.50 and 5.09 nmol/g for NPEOs and NP, respectively. The effects of particles, light and microorganism on the dissipation of NPEOs in the river water were investigated based on lab-scale experiments. When natural particles were removed, 72% and 22% degradation of NPEOs were achieved at 120 h in non-sterile and sterile conditions with light, respectively. Different concentrations of NPECs were also observed in these experiments. When suspended particle matters (SPMs) were present, about 38–50% of NPEOs were sorbed to the particulate phase in only 1 h. As a result, the degradation of NPEOs and production of NPECs were inhibited. However, the combined sorption and degradation in the presence of SPMs resulted in lower dissolved NPEO concentrations than those in the absence of SPMs. Biodegradation was the most important pathway for NPEOs degradation in the river water, while NPECs seemed to be produced through both biological and abiological pathways.

*Keywords:* Distribution; Dissipation; Nonylphenol polyethoxylates; Degradation; The Yellow River

## 1. Introduction

Nonylphenol polyethoxylates (NPEOs) are important surfactants which have been used in a wide spectrum of industrial, agricultural and domestic applications. World-wide production of NPEOs totals about 700,000 tonnes/year (Jonkers et al., 2005a), and about 60% of these surfactants finally enter natural water environment via various pathways, such as municipal or industrial wastewater discharges, and sewage treatment plant (STP) effluents (Ying et al., 2002).

Many studies have indicated that primary biodegradation of NPEOs is rapid in both STPs and natural waters (i.e. river and estuarine water), which results in an accumulation of relatively persistent small metabolites, such as nonylphenol (NP), short chain mono-, di- and tri-ethoxylates ($\mathrm{NPEO}_{1-3}$), and nonylphenoxy ethoxy acetic acids (i.e. $\mathrm{NPEC}_{1,2}$) (Field and Reed, 1996; Potter et al., 1999; Staples et al., 1999; Jonkers et al., 2001). Hence, contamination of these metabolites in aquatic environments is ubiquitous around the world (Tsuda et al., 2000; Isobe et al., 2001; Keith et al., 2001; Ferrara et al., 2001; Jin et al., 2004). Environmental concern for NPEOs has been raised due to the comparatively higher toxicity and the endocrine disrupting effects of some of these small metabolites to marine and fresh water species, and even to mammalians (Jobling and Sumpter, 1993; Laws et al., 2000).

Although the behavior of NPEOs in natural waters has been reported in some studies, their environmental degradation is still a subject of debate. Two biodegradation routes are known for these compounds (Ying et al., 2002; Jonkers et al., 2005a). One is the oxidative hydrolytic pathway, during which the main metabolites are NPECs, followed by the alkyl chain carboxylated (CAPEC) metabolites (Jonkers et al., 2001; DiCorcia et al., 1998). The other is the nonoxidative hydrolytic pathway, which results in short-chain NPEOs and NP. For example, in estuarine environments, both oxidative and nonoxidative biodegradation pathways have been reported (Marcomini et al., 1990; Jonkers et al., 2003). There also have been some

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reports on abiological degradation of NPEOs (Pelizzetti et al., 1989; Sherrard et al., 1996; Brand et al., 1998; Horikoshi et al., 2002; Goto et al., 2004). However, the mechanism about the abiological degradation process of NPEOs in natural aqueous environment is still unclear.

The Yellow River, named for its high sand content, is the second largest river in China. It is a very important water source for northern China. Lanzhou City is the second largest city in the northwest of China, and Lanzhou Reach belongs to the upper reaches of the Yellow River. Large amounts of wastewaters are discharged from the industries of Lanzhou City, which makes the river in this reach polluted heavily. However, the information on the distribution and fate of individual contaminants, especially organic pollutants, is sparse. Furthermore, degradation of NPEOs has been found to be slackened after the compounds are associated with particle phase, which may account for the persistence of NPEOs and their primary degradation products in sediments (Shang et al., 1999). This might be an important factor for governing the fate of NPEOs in the Yellow River because of its high sand content.

In summary, several aspects of the degradation behavior of NPEOs remain uncertain and, moreover, few studies have been conducted to elucidate NPEOs dissipation pathway in aqueous phase with high sand content, which is the case in the Yellow River. The objectives of this study were to assess the occurrence of NPEOs and NP in Lanzhou Reach of the Yellow River, and to investigate the degradation process and fate of NPEOs in this reach by a combination of field investigation and lab-scale experiments.

## 2. Experimental

### 2.1. Reagents and standards

Nonylphenol (NP, technical grade) was purchased from Tokyo Chemical Synthesis Ind. Co. Ltd., Japan. $NPEO_{1-15}$ and $NPEC_{1,2}$ were products of Hayashi Pure Chemical Ind. Co. Ltd., Japan. NPEOs mixture used in lab experiments was an industrial product purchased from Liaoyang Chemical Plant, China, and its component distribution is shown in Fig. 1. *n*-Hexane, isopropanol, methanol and water, which were used as mobile phase for HPLC analysis, were all of HPLC grade, and dichloromethane (DCM) used for extraction was of analytical grade.

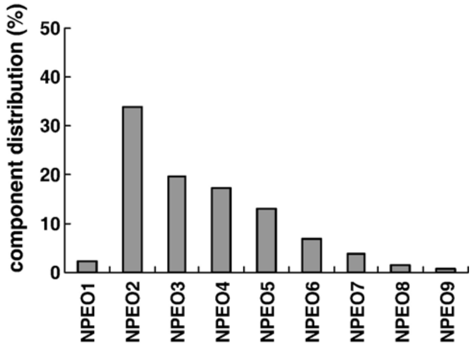

Fig. 1. Component distribution of NPEOs mixture used in the lab-scale experiments.

Table 1
Sampling sites position and some water quality parameters

| Site | Latitude/longitude | SPM (g/L) | COD (mg/L) | TOC[a] SPM/sediment (%) |
|---|---|---|---|---|
| Bapan Gorge (No. 1) | 36°08′41″N/103°25′18″E | 0.170 | 6.60 | 0.14/0.04 |
| Pipeline Bridge of Lanzhou Oil Refinery (No. 2) | 36°06′10″N/103°40′21″E | na | na | na//0.15 |
| Zhongshan Bridge (No. 3) | 36°03′51″N/103°48′52″E | 0.407 | 10.9 | 0.81/0.13 |
| Baolan Bridge (No. 4) | 36°03′11″N/103°55′58″E | na | na | na/0.45 |
| Shichuan Bridge (No. 5) | 36°09′13″N/103°59′36″E | 0.297 | 16.8 | 0.93/0.27 |

[a] TOC: total organic carbon; na: not analyzed.

### 2.2. Sampling campaign

To investigate the distribution of NPEOs in Lanzhou Reach, environmental samples (water, sediment and suspended particulate matter (SPM)) were collected at five sites, during November 8–10, 2004. The characteristics of the samples at each site are shown in Table 1. The distance from Bapan Gorge sampling site (No. 1) to Shichuan Bridge (No. 5) is about 85 km long, with the distances between each two adjacent sites being 31.70, 16.10, 13.00 and 24.75 km, respectively. During sampling time, the average water temperature was about 28 °C, with the average pH value of 8.4 and the flux of about 580 $m^3$/min. Water samples were sterilized immediately after sampling by adding 200 mg/L $NaN_3$ and stored in the dark at 4 °C. Sediment samples were stored in the dark at 4 °C before treatment.

### 2.3. Laboratory-scale experiments

In order to elucidate the effects of different environmental factors, such as SPMs, light and microorganisms, on the fate of NPEOs in this reach of the Yellow River, lab-scale experiments were conducted using 1-L glass beakers containing 1000 mL of water, which was taken from the site of Zhongshan Bridge (No. 3). Specific quantity of the stock solution of NPEOs mixture was added to each beaker, respectively. To investigate the effect of SPM, two groups of experiments were conducted, using water samples with SPM and without SPM (removed by centrifugation at 1200 r/min for 10 min). For each group, the experiments were carried out under sterile conditions without light (wrapped with aluminum foil and sterilized by 500 mg/L $NaN_3$), sterile and non-sterile conditions with light in order to differentiate the contribution of sorption, abiological degradation and biodegradation to the dissipation of NPEOs, respectively. The experiments lasted for 12 h generally, and continued to 120 h for the experiments under sterile and non-sterile conditions with light. All beakers were stirred once every 15 min during daytime. One beaker was sacrificed for analysis at certain intervals. Experiments were also conducted using river water from Bapan Gorge (No. 1) under non-sterile condition with light in the absence of SPMs.

### 2.4. Sample treatment

Water sample (1 L) was filtrated through GF/C glass fiber filters to separate SPM from the water, and then concentrated using solid phase extraction (SPE) method. The SPE was carried out using Waters Oasis™ HLB cartridge (3cc). Conditions of SPE were as follows: washed with 2.0 mL DCM/methanol (50/50, v/v), activated with 1.0 mL methanol and then equilibrated with 1.0 mL HPLC grade water. The samples were loaded to the cartridge at a flow rate of about 10 mL/min, and the cartridge was cleaned up with 1.0 mL methanol/water (95/5, v/v) and eluted with 2.0 mL DCM/methanol (50/50, v/v). The eluent was evaporated at 0.08 MPa, 50–52 °C using a rotary evaporator (RE-52AA, Shanghai Ya-Rong Biochemical Instrument Factory, China) to almost dryness, and 1.0 mL of *n*-hexane was then added to re-dissolve the residue. The solution was then analyzed by HPLC.

The solid samples (sediments and SPMs) were dried using a freeze-drier (ALPHR 1-2LD, Martin Christ Gefriertrocknunsanlagen GmbH, Germany), and then Soxhlet extracted for 24 h, using 100 mL DCM (at 53 ± 1 °C) as extraction solvent. The solvent was evaporated using rotary evaporator with temperature at 45 ± 0.5 °C. Filtration through 0.45 μm membrane was carried out before HPLC analysis.

### 2.5. Chemical analysis

Waters 1525 high-performance liquid chromatograph, with Waters 2475 fluorescence detector (Waters Company, USA) was utilized for chemical analysis in this study. A Waters W2108N007 $NH_2$ column (μBondapak™ 3.9 mm i.d. × 300 mm × 5 μm, Waters Corp., Ireland) was used for the separation of NPEOs. *n*-hexane/isopropanol (98/2, v/v) and isopropanol/water (98/2, v/v), named as solvent A and B, respectively, were used as mobile phase. 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. Injection volume was 20 μL.

HPLC was also applied to analyze NPECs concentration using a Waters $RP_{18}$ column (Symmetry Shield™ 3.9 mm i.d. × 150 mm × 5 μm, Waters Corp., Ireland). Methanol with 2 mmol/L ammonium acetate was used as mobile phase. Isocratic elution was carried out with a flow rate of 0.25 mL/min. Excitation and emission wavelengths of the fluorescence detector were 225 and 295 nm, respectively. Injection volume was 20 μL. The peaks of different NPECs could not be divided well using this method, so that total NPECs were measured as one apex in our study.

### 2.6. Quality control

Solid samples were spiked with NP and $NPEO_{1-9}$. The average recoveries and standard deviations ($n = 6$) were 99 ± 5% (NP), 97 ± 7% ($NPEO_1$), 96 ± 6% ($NPEO_2$), 102 ± 4% ($NPEO_3$), 96 ± 5% ($NPEO_4$), 99 ± 4% ($NPEO_5$), 90 ± 6% ($NPEO_6$), 95 ± 7% ($NPEO_7$), 88 ± 6% ($NPEO_8$) and 93 ± 8% ($NPEO_9$), respectively.

For water samples, the average recoveries and standard deviations ($n = 3$) of SPE process were obtained as 93 ± 4% (NP), 92 ± 4% ($NPEO_1$), 91 ± 5% ($NPEO_2$), 95 ± 4% ($NPEO_3$), 95 ± 5% ($NPEO_4$), 90 ± 6% ($NPEO_5$), 82 ± 7% ($NPEO_6$), 94 ± 5% ($NPEO_7$), 86 ± 6% ($NPEO_8$), 96 ± 5% ($NPEO_9$) and 69 ± 6% ($NPEC_s$), respectively. The low recovery of the polar NPECs was probably caused by the SPE step, as part of the analyte might remain in the water during loading through the cartridge, even if the water samples were acidified to pH of 2.

## 3. Results and discussion

### 3.1. Field investigation

#### 3.1.1. Spatial distribution of NPEOs in Lanzhou Reach of the Yellow River

The concentrations of the individual components of NPEOs in water samples at the different sampling sites are shown in Fig. 2. No long-chain $NPEO_n$ with $n > 6$ was detected in all the water samples.

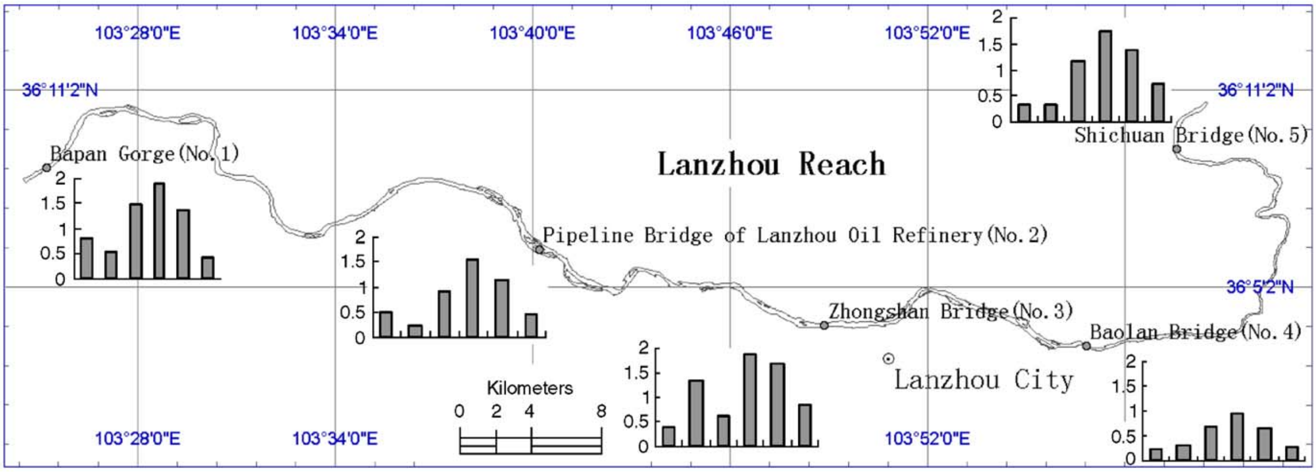

Fig. 2. Locations of sampling sites of the field investigation and NPEOs concentrations of water phase in Lanzhou Reach of the Yellow River. Unit of histogram: nmol/L. The detection limits for NP and NPEOs are 0.09 and 0.1 nmol/L, respectively.

Table 2
Occurrence of NP, NPEOs and NPECs in some aquatic environments

| Location | NP | $NPEO_{1+2}$ | $NPEO_{>2}$ | NPECs | Ref. |
|---|---|---|---|---|---|
| Glatt River | <0.3–10 | <3–69 (1EO)<br><0.3–30 (2EO) | <1–701 | <1–45 (1EC)<br>2–71 (2EC) | Ahel et al., 1994 |
| Lao-Jie River | 1.8–10 | 2.8–25.7 | | 16–292 | Ding et al., 1999 |
| Dutch estuaries | 0.03–0.93 | 0.005–1.03 | 0.03–1.3 | 0.095–1.09 | Jonkers et al., 2003 |
| Dutch coastal[a] | 1.7 | 0.73 | 35 | 0.63 | Jonkers et al., 2005b |
| Dutch coastal[b] | 0.031 | 0.14 | 0.27 | 0.11 | Jonkers et al., 2005b |
| Yellow River | 0.05–0.17 | 0.05–0.14 (1EO)<br>0.18–0.45 (2EO) | 0.7–1.5 | 0.03–0.1[c] | this study |

Unit: μg/L; (a) campaign of 1999, max-conc.; (b) campaign of 2000, max-conc.; (c) unit: nmol/L.

$NPEO_3$ concentration was the highest among the different homologues in all the water samples, with a maximum of 1.89 nmol/L detected at the site No. 3. The total concentrations of NPEOs were 6.41, 4.73, 6.77, 3.03 and 5.62 nmol/L, at different sites from the upper to the lower reaches, respectively. Compared with the result reported by other studies (Table 2), Lanzhou Reach of the Yellow River belongs to moderately polluted water for NP and NPEOs occurrence. Relatively high concentration of NPEOs was detected unexpectedly at the site of No. 1 which is located at the upstream of the city. This might be attributed to the influent of an anabranch from the upper reach, which is expected to be polluted severely (COD: 13.0 mg/L, detected on October 8th, 2004). The highest NPEOs concentration detected at the site of No. 3, which locates in the downtown area, might be explained by the discharges of domestic sewage around. The higher concentration detected at No. 5 compared to that at No. 4 is thought to be due to several discharging points from some industries and a municipal STP along this section. The relatively less NPEOs detected at the site of No. 2 and 4 suggest that natural clean-up processes exist.

Wastewaters from four large discharging points within the section from the site of No. 4 to 5 were also sampled in this work. Concentrations of NPEOs in these samples were measured as 27.64, 28.74, 35.37 and 50.20 nmol/L, which were much higher than those in water samples, especially for the 4# discharging point. The longest NPEO homologue detected in these wastewaters was $NPEO_{11}$ (Fig. 3). Hence, degradation does not only cause the reduction of total concentration of NPEOs, but also results in a shift from long-chain to short-chain $NPEO_n$. As illustrated in Figs. 2 and 3, the dominant NPEO homologue was $NPEO_5$ in wastewater; however, $NPEO_3$ was predominant in the Yellow River water. One possible reason is that the long-chain $NPEO_n$ are degraded faster than the short-chain $NPEO_n$ (Hayashi et al., 2005). In addition, short-chain $NPEO_n$ may be the degradation product of long-chain $NPEO_n$ via the nonoxidative hydrolytic pathway (Ying et al., 2002).

The concentrations of the individual homologues of NPEOs in the solid samples are listed in Table 3. Only NP and short-chain $NPEO_{n\leq 2}$ were found in the sediment and SPM samples. NP concentration was the highest, with the maximum of about 4 (SPM of No. 1 and 5) and 5 nmol/g (sediment of No. 2), respectively. In sediment samples, maximum concentrations of $NPEO_1$ and $NPEO_2$ were 0.92 (No. 5) and 0.21 nmol/g (No. 2), respectively. Contrary to the distribution in water and SPM samples, $NPEO_1$ concentrations were higher than $NPEO_2$ in sediments (except for the site of No. 2), which might be attributed to the higher lipophilicity and less degradation efficiency of $NPEO_1$. The maximum concentrations of $NPEO_1$ and $NPEO_2$ in the SPMs were 0.66 (No. 4) and 0.90 nmol/g (No. 1). In general, the concentrations in the SPMs were higher than those in the sediments, which might be explained by the larger specific surface area of SPM. No $NPEO_{n>2}$ was detected in solid phase, even though they were found in water. This is thought to be attributed to the lower hydrophobicity of NPEOs with longer EO chain. The geographic distribution of NPEOs concentration in solid phase at the different sites was different from that in water phase, which is not unexpected. Given that the sorption equilibrium cannot be reached immediately after the pollutants enter the water in the Yellow River, and the SPM contents in the water body change with the hydrographic conditions, it is understandable that the concentrations in water and solid phase might be inconsistent. And besides, the physicochemical properties of the SPMs and sediments are variable in this reach (e.g. TOC contents shown in Table 1), which can affect the distribution of NPEOs significantly. The log $K_{oc}$ ($K_{oc}$: the organic carbon normalized distribution coefficients) was calculated as 5–6 for NP and 4–5 for $NPEO_{1,2}$, which is in agreement to those measured in other studies (Van Ry et al., 2000; Ferguson et al., 2001). The higher $K_{oc}$ value of NP stems from the higher hydrophobicity of NP compared to that of $NPEO_{1,2}$. The solid–water distribution coefficient ($K_d$) in this study was calculated as $10^3$–$10^4$ L/kg for NP and $10^2$–$10^3$ L/kg for $NPEO_{1,2}$, which is lower than the values reported in other studies (Ying

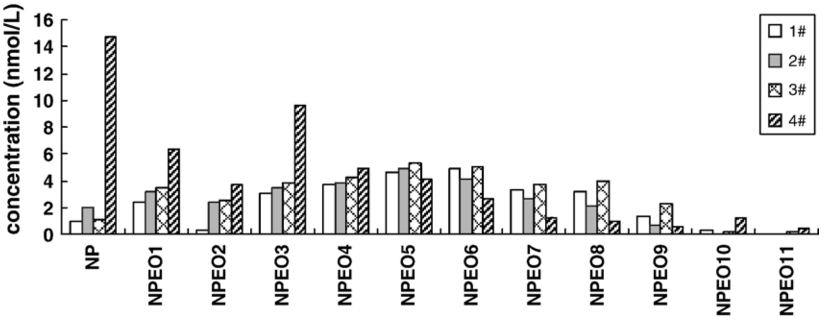

Fig. 3. NPEOs concentration of some major wastewater effluents in Lanzhou Reach. Samples of 1, 3 and 4# were industrial wastewaters, while 2# was municipal STP effluent.

Table 3
The concentration of NP and NPEOs in solid phase in Lanzhou Reach of the Yellow River

| Site | Concentration in sediment | | | Concentration in SPM | | |
|---|---|---|---|---|---|---|
| | NP | $NPEO_1$ | $NPEO_2$ | NP | $NPEO_1$ | $NPEO_2$ |
| No. 1 | 0.54 | 0.35 | 0.07 | 4.09 | 0.37 | 0.90 |
| No. 2 | 5.09 | 0.08 | 0.21 | na | na | na |
| No. 3 | 2.58 | 0.33 | nd | 2.36 | 0.37 | 0.31 |
| No. 4 | 0.28 | 0.85 | 0.13 | 3.18 | 0.66 | 0.83 |
| No. 5 | 1.48 | 0.92 | nd | 4.00 | 0.39 | 0.63 |

Unit: nmol/g dry weight; nd: not detected; na: not analyzed. The detection limits are 0.020, 0.022 and 0.017 nmol/g dry weight for NP, $NPEO_1$ and $NPEO_2$, respectively.

et al., 2002; Thiele et al., 1997). The low organic mater content of the particles in the Yellow River, which ranged from 0.04% to 0.93% (Table 1), may account for this difference. Nevertheless, the sorption of these surfactants to solid phase plays an important role in the distribution of NPEO in the Yellow River, considering the high sand content along this reach.

### 3.2. NPECs in river water

NPECs concentrations in water samples of No. 1, 3 and 5 were measured, and the concentrations were 0.05 (No. 1), 0.19 (No. 3) and 0.04 nmol/L (No. 5), respectively. A positive correlation exists between the concentrations of NPEOs and NPECs at these three sites, with the correlation coefficient ($r^2$) being 0.9667. The level of NPECs in Lanzhou Reach is much lower than those reported in other studies, compared to the NPEOs concentration in this reach (Table 2). Two reasons might be responsible for this low concentration ratio of NPEC/NPEO: (1) there was no enough time for NPEO degradation due to the relative short residence time, 6–12 h, in this reach; (2) the degradation might become more difficult because the high sand concentration helps NPEOs molecules enter the solid phase.

## 4. Lab-scale experiment

### 4.1. NPEOs dissipation under different conditions

In each of the particle-removed experiment, the concentration of NPEOs did not change much in 12 h, with total NPEOs losing 3% and 5% under sterile and non-sterile conditions with light, while there was no obvious change under sterile condition without light (Fig. 4).

Experiments under sterile and non-sterile conditions with light were continued to 120 h. Significant degradation was observed at 120 h especially under non-sterile condition, with total NPEOs concentration decreased from 4.69 to 1.33 μmol/L, resulting in the total loss up to 72%. Though the sampling points in this experiment were not enough to get the accurate dynamic data, half-life ($t_{1/2}$) and first-order rate constant ($k_1$) were calculated in order to make a comparison. The $t_{1/2}$ and $k_1$ of the total NPEOs under non-sterile condition with light were calculated as 61.5 h and 11.27 $h^{-1}$ ($r^2=0.9864$), according to the first-order dynamic equations. Comparable degradation efficiency of NPEOs in natural aquatic environments has been reported in other studies. Jonkers et al. (2001), for example, found a 4-D biodegradation efficiency of more than 99% for NPEOs in their lab-scale aerobic experiments. Light was found to be a retarding factor for biodegradation of NPEOs (Mann and Boddy, 2000). However, there are few investigations on the effect of light on abiological degradation of NPEOs. In our experiments, total NPEOs concentration decreased from 4.69 to 3.65 μmol/L in sterile condition with light. 22% of the total NPEOs disappeared from water within 120 h, with a $k_1$ value of 2.15 $h^{-1}$ ($r^2=0.9886$). The degradation of NPEOs under non-sterile conditions was much greater than that in sterile ones, which indicates that biodegradation is the most important route of NPEOs degradation in the investigated system.

When SPMs existed, a great portion of NPEOs disappeared from water within 1 h, especially for those with short EO chain (Fig. 5). This indicates that these pollutants can be sorbed to particle phase rapidly in water with relative high sand content, such as Lanzhou Reach of the Yellow River. After 1 h, the concentration of NPEOs in water almost kept constant under sterile condition without light, with 48% of the total NPEOs disappearing from water phase at 12 h (38% to 50% of different $NPEO_n$ disappeared according to different EO number). $K_d$ of $NPEO_{1-5}$ was about $1.2\times10^4$ L/kg (calculated from data of sterile treatment without light at 12 h), which is comparable to those of field investigation.

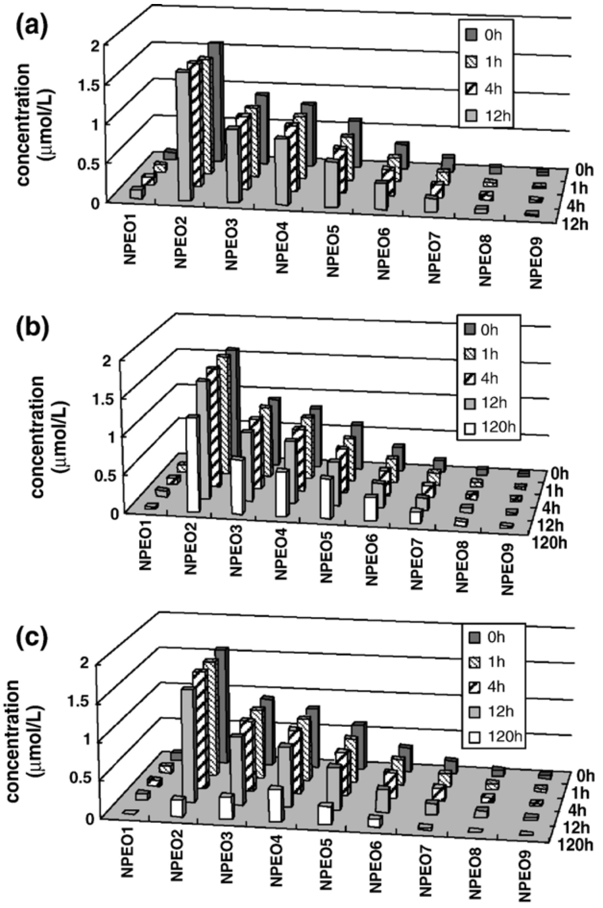

Fig. 4. NPEOs ($n=1$–9) concentration change with time under (a) sterile condition without light, (b) sterile condition with light, (c) non-sterile condition with light, in the absence of SPM.

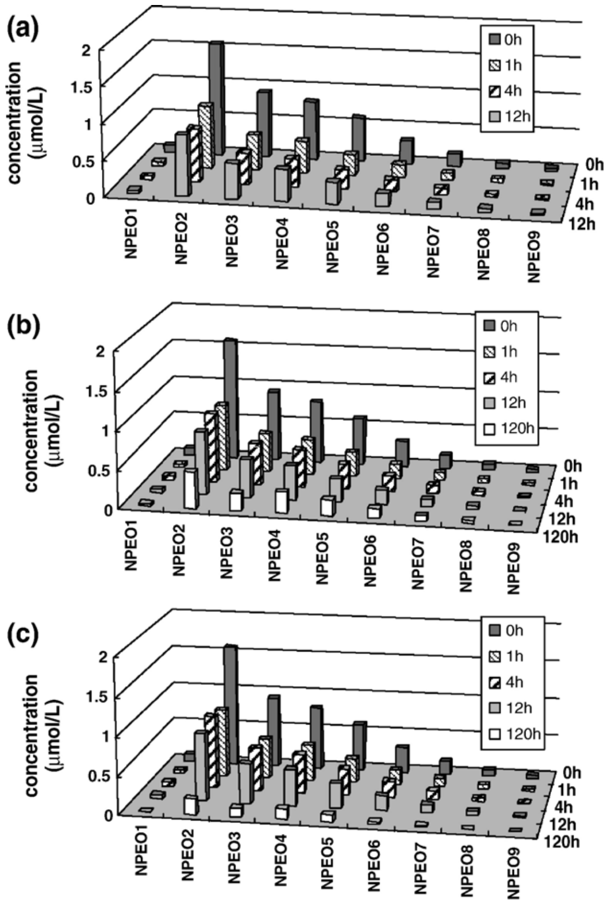

Fig. 5. NPEOs ($n$=1–9) concentration change with time under (a) sterile condition without light, (b) sterile condition with light, (c) non-sterile condition with light, in the presence of SPM in systems.

When SPMs existed, about 69% and 87% of NPEOs disappeared from water under sterile and non-sterile conditions with light at 120 h, respectively. The difference was 18%, which was much less than the corresponding difference when SPMs were removed. When SPMs were removed, 22% and 72% of NPEOs disappeared from water at 120 h under sterile and non-sterile conditions respectively, which means that the difference of about 50% of NPEOs disappearance should be ascribed to the influence of microorganisms. This seems to indicate that the sorption onto the particles suppresses the bioavailability of NPEOs. Hence, transportation of the SPM may carry the pollutants to a longer distance, though the dissolved concentration decreases fast at the contamination site.

### *4.2. Production of NPECs in different experiments*

NPECs production has been reported as an important degradation pathway of NPEOs recently (Ying et al., 2002; Jonkers et al., 2005b). In our lab-scale study, NPECs were detected to different extent in different experiments, except for the sterile treatment without light (Fig. 6).

When SPMs were removed, the production of NPECs under sterile condition with light was significant, being 24.7 nmol/L at 12 h (Fig. 6A), whereas it was negligible under dark condition. The amount of NPECs under sterile condition with light increased to $6.39\times10^2$ nmol/L at 120 h (Fig. 6B). When the activity of the organisms was not inhibited (non-sterile), the production of NPECs increased further, and the productions at 12 and 120 h were $1.06\times10^2$ and $8.81\times10^2$ nmol/L, respectively. This enhancement of NPECs concentrations could be attributed to the effect of organism. According to the experimental results, NPECs seems to be produced through both biological and abiological pathways. The abiological production of NPECs might be attributed to the photo-(catalytical) oxidation of NPEOs, as many compounds present in natural waters can act as photosensitizers, such as humic acids. These compounds can participate in the photocatalytical reactions and have strong oxidation ability to organic pollutants (Haag and Hoigne, 1985; Zepp et al., 1985; Mansour et al., 1997; Fukushima et al., 2000; Fukushima and Tatsumi, 2001).

NPECs concentrations were lower when SPM was present, being $3.53\times10^2$ and $5.56\times10^2$ nmol/L under sterile and non-sterile conditions with light at 120 h. This could be attributed to the lower availability of NPEOs in solid phase and the shielding effect of particles to light which limits the photo-oxidation. Besides, a portion of NPECs produced might have transferred to solid phase (Fukushima and Tatsumi, 2001), though $K_d$ values of NPECs are quite low.

After 120 h, $8.81\times10^2$ and $6.39\times10^2$ nmol/L NPECs were produced under non-sterile and sterile condition without SPM, while the reduction of total NPEOs concentration under these two conditions were 3.36 and 1.04 μmol/L. The amount of

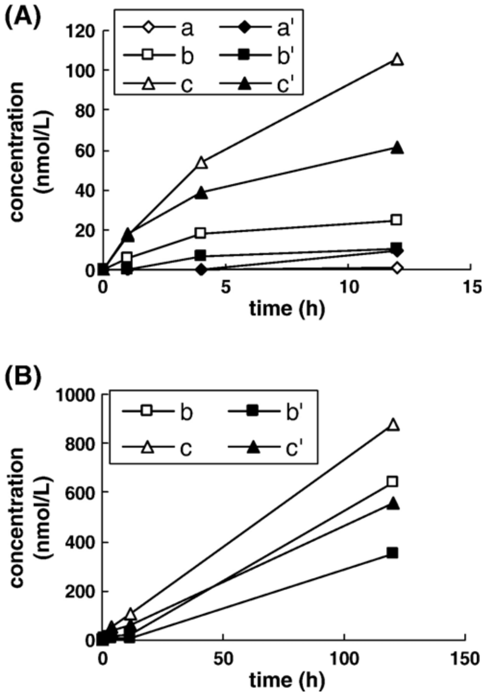

Fig. 6. NPECs concentration as a function of time within 12 h (A) and 120 h (B). (a) In sterilized treatment without light with SPM absent; (a′) in sterile treatment without light with SPM present; (b) in sterile treatment with light with SPM absent; (b′) in sterile treatment with light with SPM present; (c) in non-sterile treatment with light with SPM absent; (c′) in non-sterile treatment with light with SPM present.

NPECs production was much less compared to the amount of NPEOs degradation especially in non-sterile treatment, which means that NPEC is further degraded relatively quickly, or other degradation pathways exist.

### *4.3. NPEO degradation in water from the Bapan Gorge*

The NPEOs degradation and NPECs production in water from Bapan Gorge (No. 1) at 120 h was also measured under non-sterile condition with light in the absence of SPM. The degradation efficiency of total NPEOs at 120 h was only 27% in water from Bapan Gorge, compared to 72% in water from Zhongshan Bridge site. The much slower degradation of NPEOs in Bapan Gorge water might be attributed to the less microbial biomass (total coliform was $0.5–0.7 \times 10^3$ mpn/100 mL for upper section and $2–3 \times 10^3$ mpn/100 mL for downtown area, based on the investigation during 2003.8 and 2004.8). The lower COD value at this site (Table 1) is also hypothesized to relate to the slower degradation, because Hayashi et al. have found that the coexistence of carbon sources played a significant role in the degradation of NPEOs (2005). With the disappearance of NPEOs, $3.17 \times 10^2$ nmol/L NPECs was detected in Bapan Gorge water at 120 h.

## 5. Conclusions

In this paper, field and laboratory studies were combined to obtain insight into the environmental distribution and dissipation of NPEOs in Lanzhou Reach of the Yellow River. The results of the field study indicated a moderate level of NPEOs and NP in this reach through water and solid samples collected from five sites. In wastewater samples, long-chain $NPEO_n$ was observed at relatively high concentrations, while river waters contained $NPEO_n$ with the EO chain length less than 6, which indicates that degradation causes both the reduction of total concentration and the shift of maximum homologues distribution of NPEOs in the river water. Only shorter ethoxymers ($NPEO_{1,2}$ and NP) were detected in sediments. The $K_d$ value of NPEOs was relatively low compared with those in other studies, because the organic mater content of the particles in the Yellow River was low. NPECs were also detected in water samples though at a relatively low level, which suggests that oxidation is one of the dissipation pathways of NPEOs in the Yellow River.

The results of the lab-scale study indicate that NPEOs can be degraded easily under a non-sterile condition with light. 72% of NPEOs disappeared from water after 120 h. A much lower degradation efficiency (22% after 120 h) was observed when the system was sterilized, which means that biodegradation is a major process occurring in the river water. The production of NPECs was observed under both sterile and non-sterile conditions but at different extent, which might suggest that NPECs were formed through both biological and abiological processes as degradation products of NPEOs. However, the ratio of NPEC production to NPEO degradation was relatively small in this study. Transfer of NPEO to the solid phase was very fast, which depressed NPEOs degradation and NPECs production.

It seems that sunlight plays a role in NPEOs abiological degradation and NPECs production. However, further research is necessary to investigate the abio-/biological degradation of NPEO in natural water.

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## References

Ahel M, Giger W, Schaffner C. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment: II. Occurrence and transformation in river. Water Res 1994;28:1143–52.

Brand N, Mailhot G, Bolte M. Degradation. Photoinduced by Fe(III): method of alkylphenol ethoxylates. Removal in water. Environ Sci Technol 1998;32: 715–2720.

DiCorcia A, Costantino A, Crescenzi C, Marinoni E, Samperi R. Characterization of recalcitrant intermediates from biotransformation of the branched alkyl side chain of nonylphenol ethoxylate surfactants. Environ Sci Technol 1998;32:2401–9.

Ding WH, Tzing SH, Lo JH. Occurrence and concentrations of aromatic surfactants and their degradation products in river waters of Taiwan. Chemosphere 1999;11:2597–606.

Ferguson PL, Iden CR, Brownwell BJ. Distribution and fate of neutral alkylphenol ethoxylate metabolites in a sewage-impacted urban estuary. Environ Sci Technol 2001;35:2428–35.

Ferrara F, Fabietti F, Delise M, Bocca AP, Funari E. Alkylphenolic compounds in edible molluscs of the Adriatic Sea (Italy). Environ Sci Technol 2001;35:3109–12.

Field JA, Reed RL. Nonylphenol polyethoxy carboxylate metabolites of nonionic surfactants in U.S. paper mill effluents, municipal sewage treatment plant effluents, and river waters. Environ Sci Technol 1996;30: 3544–50.

Fukushima M, Tatsumi K. Degradation pathways of pentachlorophenol by photo-fenton systems in the presence of iron(III), humic acid, and hydrogen peroxide. Environ Sci Technol 2001;35:1771–8.

Fukushima M, Tatsumi K, Morimoto K. The fate of aniline after a photo-fenton reaction in an aqueous system containing iron(III), humic acid, and hydrogen peroxide. Environ Sci Technol 2000;34:2006–13.

Goto R, Kubota T, Ibuki Y, Kaji K, Goto A. Degradation of nonylphenol polyethoxylates by ultraviolet B irradiation and effects of their products on mammalian cultured cells. Toxicology 2004;202:237–47.

Haag WR, Hoigne J. Photo-sensitized oxidation in natural water via OH radicals. Chemosphere 1985;12:1659–71.

Hayashi S, Saito S, Kim J-H, Nishimura O, Sudo R. Aerobic biodegradation behavior of nonylphenol polyethoxylates and their metabolites in the presence of organic matter. Environ Sci Technol 2005;39:5626–33.

Horikoshi S, Watanabe N, Onishi H, Hidaka H, Serpone N. Photodecomposition of a nonylphenol polyethoxylate surfactant in a cylindrical photoreactor with $TiO_2$ immobilized fiberglass cloth. Appl Catal B 2002; 37:117–29.

Isobe T, Nishiyama H, Nakashima A, Takada H. Distribution and behavior of nonylphenol, octylphenol, and nonylphenol monoethoxylate in Tokyo metropolitan area: their association with aquatic particles and sedimentary distributions. Environ Sci Technol 2001;35:1041–9.

Jin XL, Jiang GB, Huang GL, Liu JF, Zhou QF. Determination of 4-*tert*-octylphenol, 4-nonylphenol and bisphenol A in surface waters from the haihe River in Tianjin by gas chromatography–mass spectrometry with selected ion monitoring. Chemosphere 2004;56:1113–9.

Jobling S, Sumpter JP. Detergent components in sewage effluent are weakly oestrogenic to fish—an in vitro study using rainbow trout (*Oncorhynchus mykiss*) hepatocytes. Aquat Toxicol 1993;27:361–72.

Jonkers N, Knepper T, de Voogt P. Aerobic biodegradation studies of nonylphenol ethoxylates in river water using liquid chromatography–electrospray tandem mass spectrometry. Environ Sci Technol 2001;35: 335–40.

Jonkers N, L aane RWPM, de Graaf C, de Voogt P. Fate of nonylphenol ethoxylates and their metabolites in two Dutch estuaries: evidence of biodegradation in the field. Environ Sci Technol 2003;37:321–7.

Jonkers N, Laane RWPM, de Graaf C, de Voogt P. Fate modeling of nonylphenol ethoxylates and their metabolites in the Dutch Scheldt and Rhine estuaries—validation with new field data. Estuar Coast Shelf Sci 2005a;62:141–60.

Jonkers N, Laane RWPM, de Voogt P. Sources and fate of nonylphenol ethoxylates and their metabolites in the Dutch coastal zone of the North Sea. Mar Chem 2005b;96:115–35.

Keith TL, Snyder SA, Naylor CG, Staples CA, Summer C, Kannan K, et al. Identification and quantitation of nonylphenol ethoxylates and nonylphenol in fish tissues from Michigan. Environ Sci Technol 2001;35:10–3.

Laws SC, Carey SA, Ferrell JM, Bodman GJ, Cooper RL. Estrogenic activity of octylphenol, nonylphenol, bisphenol A and methoxychlor in rats. Toxicol Sci 2000;54:154–67.

Mann RM, Boddy MR. Biodegradation of a nonylphenol ethoxylate by the autochthonous microflora in lake water with observations on the influence of light. Chemosphere 2000;41:1361–9.

Mansour M, Feicht EA, Behechti A, Scheunert I. Experimental approaches to studying the photostability of selected pesticides in water and soil. Chemosphere 1997:39–50.

Marcomini A, Pavoni B, Sfriso A, Orio A. Persistent metabolites of alkylphenol polyethoxylates in the marine environment. Mar Chem 1990;29:307–23.

Pelizzetti E, Minero C, Maurino V, Sclafani A, Hidaka H, Serpone N. Photocatalytic degradation of nonylphenol ethoxylated surfactants. Environ Sci Technol 1989;23:1380–5.

Potter TL, Simmons K, Wu JN, Kostecki P, Calabress E. Static die-away of a nonylphenol ethoxylate surfactant in estuarine water samples. Environ Sci Technol 1999;33:113–8.

Shang DY, Macdonald RW, Ikonomou MG. Persistence of nonylphenol ethoxylate surfactants and their primary degradation products in sediments from near a municipal outfall in the Strait of Georgia, British Columbia, Canada. Environ Sci Technol 1999;33:1366–72.

Sherrard KB, Marriott PJ, Amiet RG, McCormick MJ, Colton R, Millington K. Spectroscopic analysis of heterogeneous photocatalysis products of nonylphenol- and primary alcohol ethoxylate nonionic surfactants. Chemosphere 1996;33:1921–40.

Staples CA, Williams JB, Blessing RL, Varineau PT. Measuring the biodegradation of nonylphenol ether carboxylates, octylphenol ether carboxylates, and nonylphenol. Chemosphere 1999;38:2029–39.

Thiele B, Günther K, Schwuger MJ. Alkylphenol ethoxylates—trace analysis and environmental behavior. Chem Rev 1997;97:3247–72.

Tsuda T, Takino A, Kojima M, Harada H, Muraki K, Tsuji M. 4-Nonylphenols and 4-*tert*-octylphenol in water and fish from rivers flowing into Lake Biwa. Chemosphere 2000;41:757–62.

Van Ry DA, Dachs J, Gigliotti CL, Brunciak PA, Nelson ED, Eisenreich SJ. Atmospheric seasonal trends and environmental fate of alkyphenols in the Lower Hudson River estuary. Environ Sci Technol 2000;34:2410–7.

Ying GG, Williams B, Kookana R. Environmental fate of alkylphenols and alkylphenol ethoxylates—a review. Environ Int 2002;28:215–26.

Zepp RG, Schlotzhauer PF, Sink R. Photosensitized transformations involving electronic-energy transfer in natural waterssrole of humic substances. Environ Sci Technol 1985;19:74–81.