Vertical distribution of nonylphenol and nonylphenol ethoxylates in sedimentary core from the Beipaiming Channel, North China

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Abstract

The vertical profiles of nonylphenol (NP) and nonylphenol ethoxylates (NPEOs) were investigated in a sediment core from the Beipaiming Channel, North China using high sensitive LC-MS and GC-MS methods. In this core, relatively high concentrations of NP and NPEOs occurred in the surface sediment ($\leqslant 40$ cm), with the maximum value of NP and NPEOs reaching 3539 and 12735 ng/g, respectively, whereas, no NP or NPEOs were detected in deeper sediments (>40 cm). The high concentrations of NP and NPEOs in the surface layers suggested recent inputs in this area. NPEOs with short ethoxy chains (NP_nEO, $n=0$–3) were dominant in the NPEO mixture with percentages from 54% to 78%, which were similar to the distribution of homolog NPEO in effluents from nearby sewage treatment plants (STPs), indicating that the channel received the effluents from these STPs. The sewage treatment ratio was quite similar to that found in North America before the 1980s. Finally, the concentrations of NP and NPEOs were related to the total organic carbon (TOC) ($p<0.001$), suggesting that TOC was an important factor for vertical distribution of NPEOs and NP from the Beipaiming Channel.

Key words: nonylphenol; nonylphenol ethoxylates; sediment core; Bohai Bay

Introduction

Nonylphenol ethoxylates (NPEOs) are important non-ionic surfactants widely used in industrial and consumer products as cleaning agents and emulsifiers (Warhurst, 1995; Naylor, 1996). A typical NPEO surfactant formulation is comprised of NP with an average of 10 ethoxy units, usually within the range of 1 to 20 ethoxy units. Biodegradation of NPEOs during wastewater treatment processes can result in shortening of the ethoxy chain and subsequent degradation to NP under anaerobic conditions (Ahel and Giger, 1993; Ahel et al., 1994a, b; Giger and Brunner, 1984). Considering the estrogenicity and the large production volumes of NPEOs and NP (Servos, 1999; Jobling et al., 1996; Sharpe et al., 1995; White et al., 1994), there is an increasing concern about the environmental occurrence and fate of NPEOs and their biodegradation intermediates.

Many studies have shown that NP and NPEOs are ubiquitous in aquatic environments (Maruyama et al., 2000; Kannan et al., 2003), as exemplified by their occurrence in sediment and fish tissues (Shao et al., 2005; Keith et al., 2001; Lye et al., 2001; Rice et al., 2003; Ferrara et al., 2001). It has been found that NPEOs and their neutral metabolites accumulate and persist in sediments, and their half-lives are about 60 years in the stratified sediment (Shang et al., 1999). Thus, the vertical profiles of NP and NPEOs in sediment cores can be used to evaluate their history in local areas as exemplified by the bedded sediment in a sewage-impacted urban estuary (Shang et al., 1999; Ferguson et al., 2003). However, there is insufficient information about the vertical profiles of NPEOs and NP in sedimentary samples, especially in China (Hu et al., 2005).

Bohai Bay is a semi-enclosed shallow water basin located in the north of China. Beipaiming Channel, located on the western shore of Bohai Bay, receives industrial and municipal wastewaters from the Tianjin Economic-technological Development Area (TEDA), which is one of the most industrialized areas and is a probable source of NP and NPEOs entering Bohai Bay.

In a previous study, relatively high concentrations of NPEOs and NP were found in Bohai Bay, which were attributed to high loading of NPEOs from estuaries adjacent to Bohai Bay (Hu et al., 2005). In this article, the vertical profiles of NP and NPEOs in a sedimentary core from Beipaiming Channel were investigated, to determine the input in this area, which will contribute to the evaluation of their loading in Bohai Bay.

1 Materials and methods

1.1 Sediment sampling

Fig.1 shows a map indicating the place where a sediment core was taken from, in Beipaiming Channel (39°30′N, 117°26′E), in November 2001. The core sample was sliced at 5-cm intervals for up to 145 cm, with a clean stainless steel slicer. Each section was stored at –20°C until analysis.
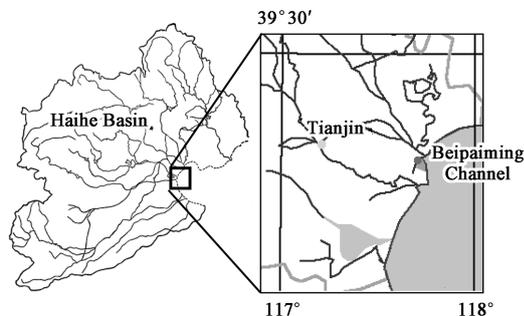

Fig. 1 Location of the sediment core from Beipaiming Channel, China.

1.2 Chemicals and standards

NP (technical grade), a mixture of compounds with branched side chains, was purchased from Kanto Chemicals (Tokyo, Japan). Authentic standard nonylphenol mono-(NP_1EO), di-(NP_2EO), tri-(NP_3EO), tetra-(NP_4EO), penta-(NP_5EO), and hexaethoxylates (NP_6EO) and mixture standard of NP_9EO (a mixture of NPEOs with an average of 9 EO units) and $NP_{15}EO$ (a mixture of NPEOs with an average of 15 EO units) were purchased from Hayashi Pure Chemicals (Tokyo, Japan). Dichloromethane, methanol, acetonitrile, and hexane were HPLC grade (Fisher Chemical Co., China). Ultra pure water was prepared using an Easypure UV Compact Ultrapure System (Fisher Chemical Co., China).

1.3 Sediment extraction and analysis

1.3.1 Extraction

For Soxhlet extraction, sediment (10 g dw mixed with 20 g Na_2SO_4) was transferred to a quartz extraction thimble and extracted with 250 ml of dichloromethane/methanol (7:3, v/v) for 24 h. Extracts were passed through 12 g of 5% H_2O deactivated neutral Al_2O_3 (200 mesh size, Shanghai Ludu Chemicals, China) packed in a glass column (10 mm i.d.) for cleanup and fractionation. The first fraction, eluted with 30 ml high-purity hexane and 30 ml hexane/dichloromethane (3:1, v/v), contained some nonpolar or less polar chemicals. NP and NPEOs were eluted in the second fraction with 30 ml hexane/dichloromethane (50:50, v/v), 40 ml dichloromethane, 30 ml dichloromethane/methanol (85:15, v/v), and 30 ml dichloromethane/methanol (50:50, v/v). NP, NP_1EO, and NP_2EO were determined by gas chromatography-mass spectrometry (GC-MS). NPEOs were analyzed using liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS) (Shao *et al.*, 2002).

1.3.2 Chemical analysis

GC-MS analysis was performed with a Hewlett-Packard

5890 gas chromatograph connected to a Hewlett-Packard 5971 mass spectrometer. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. The injector temperature was maintained at 250°C, and the detector source temperature was kept at 280°C. A DB-5MS capillary column (30 m 0.25 mm i.d. with a film thickness of 0.25 μm) was used for NP, NP_1EO, and NP_2EO analysis, programmed to progress from 50°C (2 min) to 200°C at 20°C/min (2 min), and to 260°C at 5°C/min, and then to 280°C at 20°C/min (5 min). The injection volume was 2 μl, and a splitless mode was used. Quantitative analysis was performed using the selected ion monitoring mode, and the fragment ions were selected according to the most abundant ions in each oligomer.

NPEOs with $n>2$ were detected with the help of LC-ESI-MS being performed using an Alliance 2690 HPLC (Waters, USA) equipped with a quaternary gradient pump, an autosampler with a 100-ml injection loop, a C_{18} precolumn (2.1 mm in ID×50 mm, 3 μm Capcell Pak, Shiseido, Japan), and a silica analytical column (2.1 mm in ID×150 mm, 3 μm Spherisorb SW3, Waters). The flow was kept at 0.1 ml/min for 1 min with 100% acetonitrile, and then increased linearly to 0.35 ml/min over 34 min. The solvent composition was changed linearly to 75% acetonitrile/25% water over 35 min, then linearly to 100% acetonitrile over 5 min, while the flow was kept at 0.35 ml/min for 10 min. The flow was then held at 0.1 ml/min for 40 min to equilibrate the columns before the next injection. A platform ZMD single quadrupole mass spectrometer (Micromass, Manchester, UK) was used, with a Z-Spray ion source, fitted with a pneumatically assisted electro-spray probe. NPEOs were detected in the positive mode, and typical ion source parameters were used as follows: ESI capillary voltage at 3.5 kV; extractor voltage at 5 V; source block temperature at 120°C; desolvation temperature at 180°C; ion energy at 0.8 V; multiplier voltage at 650 V; nitrogen was used as a desolvation gas, with a flow rate between 270 and 350 L/h, and cone gas at a flow rate of 70 to 100 L/h. The cone voltage was ramped from 25 to 70 V with the full scan mass ranging from 280 to 1500 and with a scan time of 1.2 s. Masslynx 3.4 workstation software was used for data processing. Quantitative analysis was performed using the ions of $[M+Na^+]$ (Na^+ adducted molecules with NPEOs). The procedure described above was validated for recoveries (ranging from 92% to 105% for NPEOs and 80% for NP). The precision was estimated at better than 20% based on the analysis of three replicate samples collected from the Beipaiming Channel.

1.4 Total organic carbon

Total organic carbon (TOC) was measured by the high-temperature combustion method. Dry sediment (about 5 mg) was put into small precombusted (600°C, 4 h) quartz sample boats. Phosphoric acid (20%) was added to remove inorganic carbon from the samples. Finally, the samples were analyzed using a TOC Analyzer (Apollo 9000, Tekmar-Dohrmann, USA).

2 Results and discussion

2.1 Vertical profiles of NP and NPEOs in a sedimentary core from Beipaiming Channel

Fig.2 shows the vertical profiles of NP and NPEOs in the sediment core. NP concentrations ranged from no detection to 3539 ng/g dry weight (dw), which is higher than those reported in the Cuyahoga River (Rice *et al.*, 2003) and Nanpaiwu River (Hu *et al.*, 2005). It was found that although the NP concentration was less than the undetectable level at the depth of 145 to 40 cm, within the surface layer (≤40 cm) the concentration was from 579 to 3539 ng/g dw. The maximum value occurred at 25–30 cm followed by 3209 ng/g dw at a depth of 5–10 cm. This profile was similar to that in a sediment core from Jamaica Bay (Ferguson *et al.*, 2003). Not surprisingly, the concentration profile of NPEOs in the core also showed a distribution similar to that of NP in the same samples (Fig.2b), as also the NPEOs were only detected within 40 cm from the surface sediment, and the total NPEO concentration ranged from 736 to 12735 ng/g dw. The maximum concentration of NPEOs occurred in the 0–5 cm layer with the maximum of 12735 ng/g dw, which was followed by 4446 ng/g dw at the depth of 25–30 cm. The above vertical profiles for NPEOs and NP reflected the recently increased inputs of NPEOs in this area. The fact that there have been many new electronic and chemical corporations established in the TEDA since 1984, and also the fact that the Beipaiming Channel was dug in 1985, to receive industrial and domestic wastewater, is strong evidence that NP and NPEOs could only be detected in the surface sediment (<40 cm).

Fig.3 shows the relationship between the concentration of NPEOs and NP in the sediment. The NP concentrations in the sediment appeared to increase with an increase in NPEO concentration in the sediment from the Beipaiming Channel ($p<0.001$). This result indicates that the occurrence of NP is related to NPEOs. In the previous article, similar results were also found in other sediment core samples from the Nanpaiwu River, another estuary adjacent to Bohai Bay (Hu *et al.*, 2005).
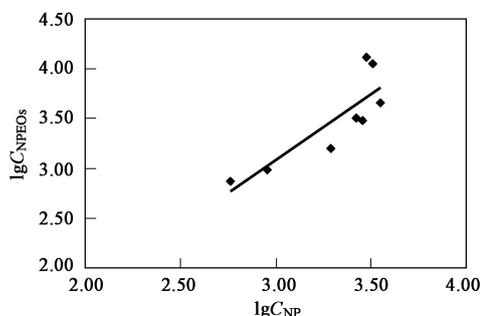

Fig. 3 Relationship between the concentration of NP and NPEOs in the sedimentary core from Beipaiming Channel, China ($p<0.001$, $r^2=0.7087$).

2.2 Distribution of homolog NPEOs in NPEO mixture

Nonylphenolic compounds are generally divided into three groups: (a) NP, (b) $NP_1EO + NP_2EO$, and (c) NP_3EO–$NP_{18}EO$. The typical distributions of homolog NP_nEO ($n=0$–8) in the NPEO mixtures at different depths are shown in Fig.4. In contrast to the commercial mixture, the contributions of NP_1EO, NP_2EO, and NP are significantly higher than those in the long ethoxy chain NP_nEO ($n=3$–18) in this sedimentary core. As shown in Fig.4a, NP_1EO and NP_2EO in the 0–5 cm layer were the prominent components of the total NPEO mixture (48%), and NP also significantly contributed 19%. However, in the deeper sediments (20–25 cm), a considerable contribution
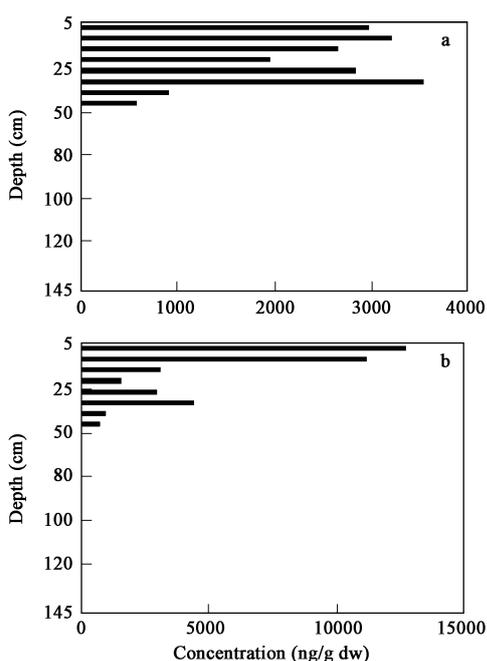

Fig. 2 Concentration profiles of NP(a) and NPEOs(b) in sedimentary core from Beipaiming Channel.
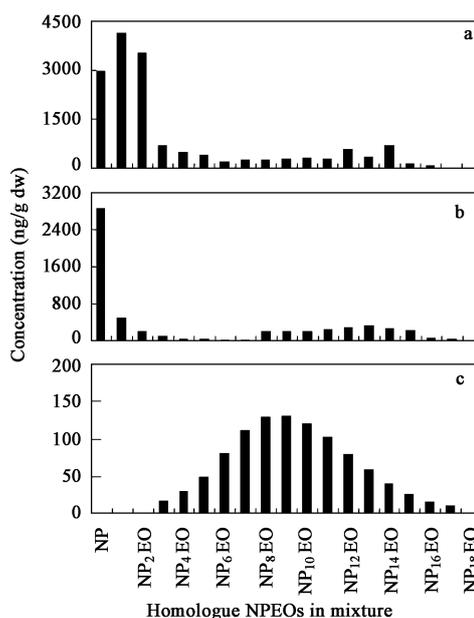

Fig. 4 NPEO homolog distribution at different depths from the Beipaiming Channel. (a) 0–5 cm; (b) 20–25 cm; (c) commercial NP_9EO (1000 ng/g).

(49%) to the total was from NP, which was significantly higher than those of NP$_1$EO (8%) and NP$_2$EO (3%) (Fig.4b). Generally, two types of homolog distributions were observed in this core; that is, in the recently deposited sediments ($\leqslant$10 cm), NPEOs were dominated by NP$_1$EO and NP$_2$EO, whereas in the deeper sediments (>10cm), an NP-rich NPEO mixture was present.

It is well-known that NP$_n$EO (n=0–2) are the predominant metabolites of NPEOs through biodegradation (Ahel and Giger, 1993; Ahel *et al.*, 1994a, b). Therefore, it can be hypothesized that the characteristic distribution dominated by NP$_n$EO (n=0–2) in this sedimentary core may be on account of the output from STPs or the biotransformation between the long and short ethoxy chains in the estuarial environment. Ahel *et al.* (1994a) investigated the patterns of NPEOs in the effluents from 11 different STPs, and found that the NPEO mixtures from 10 STPs were dominated by NP$_1$EO and NP$_2$EO, whereas, NP dominated that from one STP. Such a difference in NPEO patterns was explained by the different operating conditions of individual STPs (Ahel *et al.*, 1994a). In addition, Ahel *et al.* (1994b) also reported that the biodegradation efficiency of NPEOs in rivers is much lower than that in STPs. Thus, a similar distribution in those in the effluents of STPs and their persistence in the sediment suggested that NPEOs and NP in the channel would stem from the discharging of sewage effluent from STPs.

The ratio of NP$_n$EO (n=0–3) to total NPEOs has been used as a marker for the sewage treatment ratio (Ferguson *et al.*, 2003). To estimate the sewage treatment ratio of NPEOs in this area, the ratio with other countries has been compared. In this core, the ratio of NP$_n$EO (n=0–3) to total NPEOs ranges from 54% to 78% (Table 1). Although the age of sediments has not been measured in this study, the sediment at 40 cm corresponds to the one from 1985, when the channel was dug.

Ferguson *et al.* (2003) reported that the ratio in sediments of Jamaica Bay, North America, was from 86% to 95% in the period 1980–1995, 77% to 86% in the period 1963–1980, and 43% to 49% before 1963. Compared to the ratio in Jamaica Bay, the sewage treatment ratio in this area is quite near to that in North America before the 1980s. Because of the low sewage treatment ratio, most of the industrial wastewater was discharged into the channel without biological treatment. In fact, although the amount of sewage was 900000 m^3/d, the capacity of the STP was 100000 m^3/d in this area with the ratio of treatment of 10%.

2.3 Relationship between TOC and NP, NPEOs in sedimentary core

TOC values of the sedimentary samples varied from 0.93% to 2.40%. For the sedimentary samples, a relationship between the NP concentration and TOC was plotted in Fig.5a. It was found that the NP concentration increased with increasing TOC in the sedimentary core, and the regression analysis indicated that this correlation was statistically significant (p<0.001). A good correlation was also obtained between the NPEOs concentration and TOC (p<0.001) (Fig.5b). These results indicated that the organic carbon in the sediments was an important factor for vertical distribution of NPEOs and NP from the Beipaiming Channel.

3 Conclusions

A relatively high concentration of NP and NPEOs was detected in the surface sediment of a sedimentary core from Beipaiming Channel, suggesting a recent increasing input of these compounds in this area. The vertical distribution of NPEOs was found to be quite similar to that of NP in the same samples, and the significant correlation between the concentration of NPEOs and NP demonstrated that the occurrence of NP is related to that of NPEOs in the sediment from the Beipaiming Channel. The short chain NPEOs dominant in NPEO mixtures in this sedimentary

Table 1 Concentrations (ng/g dw) of NPEOs with EO units ranging from 0 to 18 in sedimentary core from Beipaiming Channel

Chemicals	Depth (cm)								
	5	10	15	20	25	30	35	40	50
NP	2976	3209	2661	1951	2843	3539	906	579	ND
NP$_1$EO	4126	4146	404	166	492	1553	139	97	ND
NP$_2$EO	3516	2222	271	231	195	1087	95	32	ND
NP$_3$EO	697	697	269	132	109	84	31	ND	ND
NP$_4$EO	492	232	128	23	37	145	7	73	ND
NP$_5$EO	410	193	107	19	31	121	6	60	ND
NP$_6$EO	203	207	102	26	14	106	31	69	ND
NP$_7$EO	254	249	116	71	14	126	55	92	ND
NP$_8$EO	252	320	203	112	202	184	85	108	ND
NP$_9$EO	299	299	210	127	215	204	145	91	ND
NP$_{10}$EO	311	325	231	171	200	211	159	50	ND
NP$_{11}$EO	304	333	180	157	236	140	83	22	ND
NP$_{12}$EO	570	430	217	133	279	129	61	28	ND
NP$_{13}$EO	353	729	319	144	326	166	64	13	ND
NP$_{14}$EO	711	418	192	50	274	120	18	2	ND
NP$_{15}$EO	144	273	138	22	221	50	2	ND	ND
NP$_{16}$EO	83	70	38	4	70	15	ND	ND	ND
NP$_{17}$EO	8	23	15	1	34	4	ND	ND	ND
NP$_{18}$EO	2	2	3	ND	10	1	ND	ND	ND
R^*	0.72	0.71	0.62	0.7	0.63	0.78	0.62	0.54	ND

*R = $\sum$NP$_n$EO(0–3)/$\sum$NP$_n$EO(0–18).
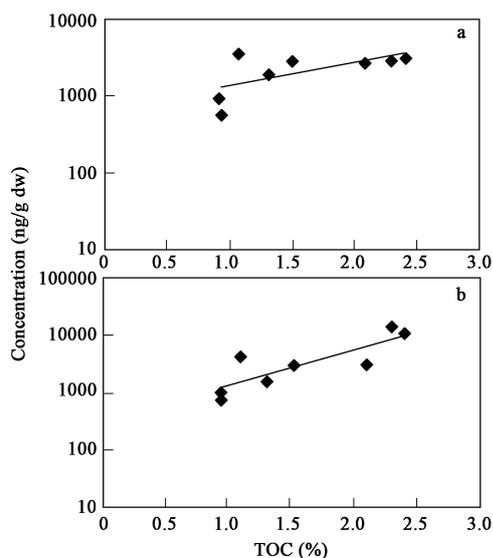
Fig. 5 Relationship between NP and NPEOs concentrations and TOC in the sedimentary core from Beipaiming Channel. (a) NP ($p<0.001$, $r^2=0.4143$); (b) NPEOs ($p<0.001$, $r^2=0.71$).

core indicated that the channel received some effluents from STPs, and the sewage treatment ratio is relatively low in this area.

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