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Nonylphenol and Nonylphenol Ethoxylates in River Water, Drinking Water, and Fish Tissues in the Area of Chongqing, China

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Abstract. Little attention has been paid to the estrogenic-like compounds, such as 4-nonylphenol (4-NP) and its potential precursor nonylphenol ethoxylates (NPEOs), in China although its usage is huge. Water samples and corresponding drinking water samples were seasonally collected at five sites of each of the two main rivers in Chongqing Area. Individual nonylphenol ethoxylates (NPEOs) and 4-NP in the Changjiang River and Jialingjiang River were detected by normal-phase liquid chromatography electrospray ionization mass spectrometry and gas chromatography-mass spectrometry. The results indicated that of the five sampling points in the two rivers, NPEOs were the dominant pollutant in April and December with the similar distribution profile, and total NPEOs with different ethylene oxide lengths were 6.9–97.6 μg/L in April and 2.5–52.7 μg/L in December. However, NP was the dominant pollutant in July with a concentration of 1.7–7.3 μg/L. Corresponding drinking water samples derived from river water as source suggested that the conventional water treatment process used in the five waterworks could remove NPEOs from the source water with high removal efficiency (>99%). The 4-NP removal efficiency, however, varied in a range of 62% to 95%, leaving a significantly high concentration of NP (0.1 to 2.7 μg/L) in drinking water in July. Fish samples taken in December 2000 contained 4-NP of ∼1.9μg/g and NPEOs of 0.4–48.3μg/g, with the highest concentration level found in liver.

Recent studies have demonstrated that compounds such as short nonylphenol ethoxylates (NPEOs) homologues, carboxylated metabolites and 4-nonylphenol (4-NP) could exert estrogenic effects on aquatic fish, mammals, and birds (White *et al.* 1994; Sharpe *et al.* 1995; Jobling *et al.* 1996; Servos, 1999). *In vivo* bioassay studies have shown that gestational and lactational exposure of male rats to octylphenol ethoxylates with five-unit EO chains results in reduced testicular size and sperm production (Sharpe *et al.* 1995). There is increasing evidence that the above intermediates are capable of inducing synthesis of the yolk protein vitellogenin in male rainbow trout (Blackburn and Waldock 1995; Harries *et al.* 1996). Although these compounds elicit lower estrogenic potency than the natural hormone, the significance of exposure to these biodegradation intermediates should not be neglected, since they are prevalent in the environment.

The occurrence of NPEOs and intermediates in water and sediment in the United States, Europe, and Japan has been well documented (Naylor *et al*. 1996; Kannan *et al*., 2003; Ahel *et al.* 1994; Di Corcia *et al.* 2000; Maruyama *et al.* 2000, Thiele *et al.* 1997). Recently, several studies have examined the residues of 4-NP and NPEOs with short EO units ($n < 6$) in fish (Rice *et al.* 2003; Tsuda *et al.* 2000; Keith *et al.* 2001; Lye *et al.* 1999; Ferrara *et al.* 2001; Kannan *et al*., 2003). To date, there is no documented evidence of the existence of NPEOs with more than 5 units in fish.

The annual output of alkylphenol ethoxylates (most of which are NPEOs) in China is estimated to be about 50,000 tons (Huang 1998). In some countries, the above compounds pollute the aquatic environments mainly through the discharging of sewage treatment effluents, with NP2EC and NP1EC usually the dominant products, followed by NP2EO, NP1EO, and 4-NP (Jonkers *et al.* 2001; Di Corcia *et al.* 2000); in China, point sources are the dominant contributor of the compounds because of the low sewage treatment ratio (the volume ratio of treated sewage to and the total discharged sewage), which is reported to be less than 35% in 2002 in China (http://www.cin.gov.cn/indus/speech/2001072303). Notwithstanding the large annual output of NPEOs, little information is available on the environmental behavior of NPEOs and the related compounds in China. A comprehensive analytical method based on normal-phase liquid chromatography electrospray ionization mass spectrometry (NPLC-ESI-MS) has been established in our lab for determination of NPEOs with the whole chain length in the aquatic environment (Shao *et al.* 2002a). In this paper, we first document the occurrence and seasonal changes of NPEOs and their intermediates in the Changjiang and Jialingjiang rivers in Chongqing City, China. The residual concentrations of these compounds in drinking water and fish were also detected to

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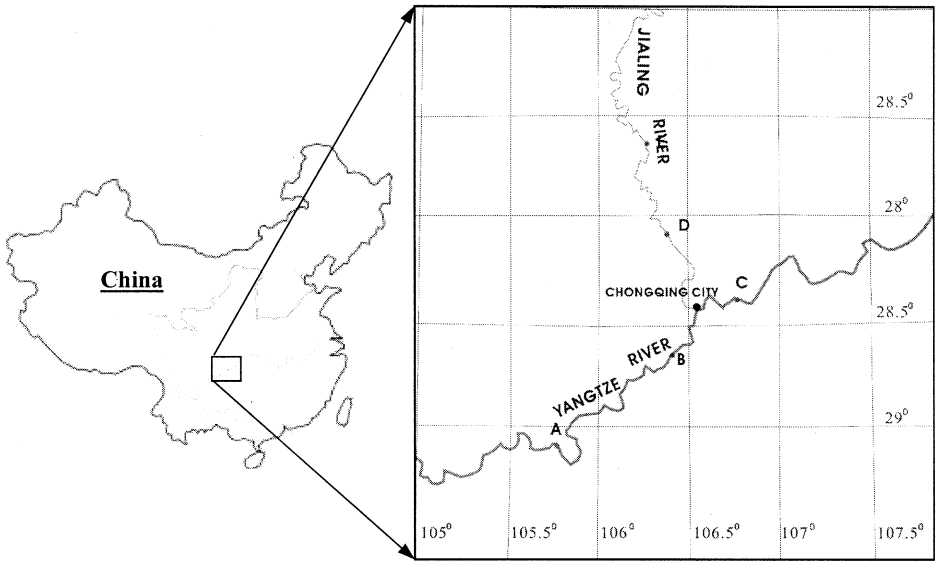

Fig. 1. Distribution of sampling sites

provide information on the dietary exposure of humans. Changjiang River, the largest river and most important water resource in China, provides fresh water with a capacity of 10^{12} m^3 per year. Chongqing City, the most important industrial city upstream of the Changjiang River, affects the water quality of the river to a large extent with its huge population (30 million) and industrial output. Because of this, the information from our research is very important to the policymakers in China to evaluate the risks of this group of chemicals.

Materials and Methods

Materials

4-Nonylphenol (technical grade), a mixture of compounds with branched side chains, was purchased from Kanto Chemicals (Tokyo, Japan). Authentic standard nonylphenol mono- (NP1EO), die- (NP2EO), and tri- (NP3EO), tetra- (NP4EO), penta- (NP5EO), hexaethoxylates (NP6EO) and mixture standard of NP9EO (a mixture of NPEOs with an average of nine EO units) and NP15EO (a mixture of NPEOs with an average of 15 EO units) were purchased from Hayashi Pure Chemicals (Tokyo, Japan). Standard stocking solutions were prepared in acetonitrile.

Methylene chloride, acetonitrile, and methanol were all high-performance liquid chromatography (HPLC) grade obtained from Fisher Chemicals Co. (Beijing, China). Ultrapure water was made by the Easypure UV compact ultrapure system (Barnstead Internatinal Dubugue, IA) at a resistivity of 18.3 MΩ/cm. Supleclean ENVI-Carb solid phase extraction cartridges (GCB) and a 6 × 1.4-cm i.d. polypropylene tube (500 mg) were purchased from Supelco (Bellefonte, PA) for sample preparation. All the glassware are rinsed with n-hexane and acetone of pesticide residue grade and then baked in muffle at 400°C for 4 h before use to avoid contamination.

Sample Collection and Preparation

Chongqing City, one of the most important industrialized cities in China, is surrounded by the Changjiang River and the Jialingjiang River (which eventually flows into the Changjiang River). The two rivers are used as the water source for the Chongqing area. As shown in Figure 1, sites A and E were located upstream of the Changjiang River and sites B and D were downstream of the Jialingjiang River. Site C was the converging site of the two rivers. Sampling on the five sites was conducted in April 28, July 28, and December 26, 2000, respectively. The corresponding water temperatures were about 12, 28, and 15°C, respectively. The river samples were taken from the water intake of the respective waterworks, and the samples of drinking water were from the distribution tank of each waterworks. All of the five waterworks use the conventional coagulation/sedimentation/sand filtration process for drinking water production. The samples were collected into precleaned glass bottles and prepared immediately after collection. Otherwise, 1% of formaldehyde was added to prevent microbial degradation and the samples were stored at 4°C in the dark. For further investigation on the possible bioeffect, fish samples (*Coreius Guichenoti, Coreius heterodon, Leptobotia elongata, Rhinogobio Typu, Rhinogobio ventralis)* and corresponding river water from the two rivers were taken on December 26, 2001. Unfortunately, fish samples from sites A, C, and E were not available in spite of the efforts in sample taking. Sediment samples were not available because the river bottoms are composed of cobblestones and fine-grained sands.

The sample extraction method proposed by Di Corcia *et al*. (1998, 2000) was used with minor modification. Briefly, water samples (1 L) were filtrated by a 0.45-μm glass fiber filter paper (Millipore Co., Bedford, MA, USA). The filter paper was soaked in 100-ml methanol/water (50:50,vol/vol) solution for 2 h, and then ultrasonicated for 30 min. The acquired solution was mixed with filtrate before extraction. A GCB cartridge was conditioned sequentially with 10 ml of methylene chloride/methanol (80:20, vol/vol), 6 ml methanol, and 6 ml water with pH = 3. The acidified sample (pH = 3) was passed through a GCB cartridge with a flow rate of 10–15 ml/min, and a 100 ml 50% methanol/water mixture used for washing the reservoirs was also passed through the cartridge. An additional 10 ml of water was applied to wash the walls of the cartridges. The residual water was removed by passing a gentle nitrogen stream through the cartridges for about 10 min. NPEOs were desorbed from the cartridges by 10 ml methylene chloride/methanol (80:20, vol/vol). Finally, the residues were dried under a gentle nitrogen stream, and reconstituted with 2 ml of ion reagent, an acetonitrile/water (95:5,vol/vol) solution containing 1 mmol/L sodium acetate.

For fish samples, 0.5 g each of muscle, liver, and gill (wet weight) were mixed with 15 g anhydrous sodium sulfate and Soxhlet extracted with a solvent mixture of methanol/methylene chloride (3:7) for 14 h.

The extract was rotary evaporated to a volume of 1 ml and then transferred to a flask with 4 × 100 ml water. The solution was rinsed with a GCB SPE cartridge using the same procedure based on Di Corcia's extraction method.

Analysis

The final extracts were measured using the LC-ESI-MS methods and GC-MS previously described (Shao *et al.* 2002a, 2002b). NPEOs with n > 2 were detected by LC-ESI-MS. A platform ZMD single quadrupole mass spectrometer (Micromass, Manchester, U.K.) was used with a Z-Spray ion source fitted with a pneumatically assisted electrospray probe. NPEOs were detected in the positive mode, typical ion source parameter 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 desolvation gas with flow between 270 and 350 l/h and cone gas at the flow 70–100 l/h; the cone voltage ramped from 25 to 70 V with the full scan mass ranged from 280 to 1500 with a scan time of 1.2 s. Masslynx 3.4 workstation software (Waters Corp; Milford, MA). was used for data processing.

The qualitative identification of target compounds was done in full-scan mode by matching time and the mass spectrum with standards. Quantitative analysis was performed using selected ion monitoring in order to achieve maximum sensitivity. A series of five standard solutions were prepared by diluting the standard stock solution. For NPEOs with n > 6 without authentic standards, the concentration in the environmental samples was determined by external calibration using NP9EO as a mixture standard. The composition of the environmental samples was determined by analyzing the molar distributions of individual NPEOs in NP9EO or NP15EO and by using HPLC-UV at 277-nm UV absorbance, assuming that each homologue had the same molar adsorption coefficient as described in our previous paper (Shao *et al.*, 2002a). For NPEOs with n < 6, pure standard compounds were used to find the calibration curve.

4-NP, NP1EO, NP2EO were measured with GC-MS for their low sensitivities upon using LC-ESI-MS. The specific method was described in a previous report (Shao *et al.* 2000b). Briefly, operation was performed on a GC-MS (5890SeriesII GC, 5971 MSD, Hewlett-Packer, USA) with a HP-5-MS column (0.25-mm i.d. × 30 m in length, 0.25 μm). Injection port and detector interface temperatures were 230°C and 280°C, respectively. Carrier gas (helium) linear velocity was held constant at 40 cm/s. The electron energy and electron multiplier voltage were 70 eV and 2000 V, respectively. The injector was carried out in splitless mode with 2-μl injection volume. The initial oven temperature was 50°C and ramped at 20°C/min to 200°C with 5-min hold time, and then ramped at 5°C/min to 260°C.

Absolute detection limits were in the low nanogram per liter range. The performance of SPE was estimated using spiking samples of all oligomers with recoveries ranging from 92% to 117% and a relative standard deviation of 2%–20%. The detection limits for water samples were estimated to be 10, 20, 50, 2, and 1 ng/L for 4-NP, NP1EO, NP2EO, NP3EO, and NPEOs (n > 3), respectively, and 5.0, 20.0, 30.0, 5.0, and 2.0 ng/g (wet weight) for fish samples.

Results and Discussion

Concentration Levels of 4-NP and NPEOs in River Samples

Figure 2 shows the distribution patterns of NPEOs and 4-NP in samples of site A located on the Changjiang River taken on April 28, July 28, and December 26, 2000. NPEOs with various EO lengths and 4-NP were detected in all samples. In the sample taken April 28 and December 26, the peaks of the NPEOs showed a pattern similar to that of standard NPEOs samples, and NP5EO and NP24EO were the main components. The fact that the 4-NP, NP1EO, and NP2EO were detected in very low levels in samples taken on April 28 and December 26 suggested that NPEOs were not subjected to significant biodegradation under the prevailing environmental conditions (water temperature, 10–15°C). The sample taken from the same site on July 28, however, showed a very different distribution pattern. 4-NP and NP1EO became the dominating species, indicating that NPEOs degraded rapidly under these conditions (water temperature, 28°C). This seasonal change of

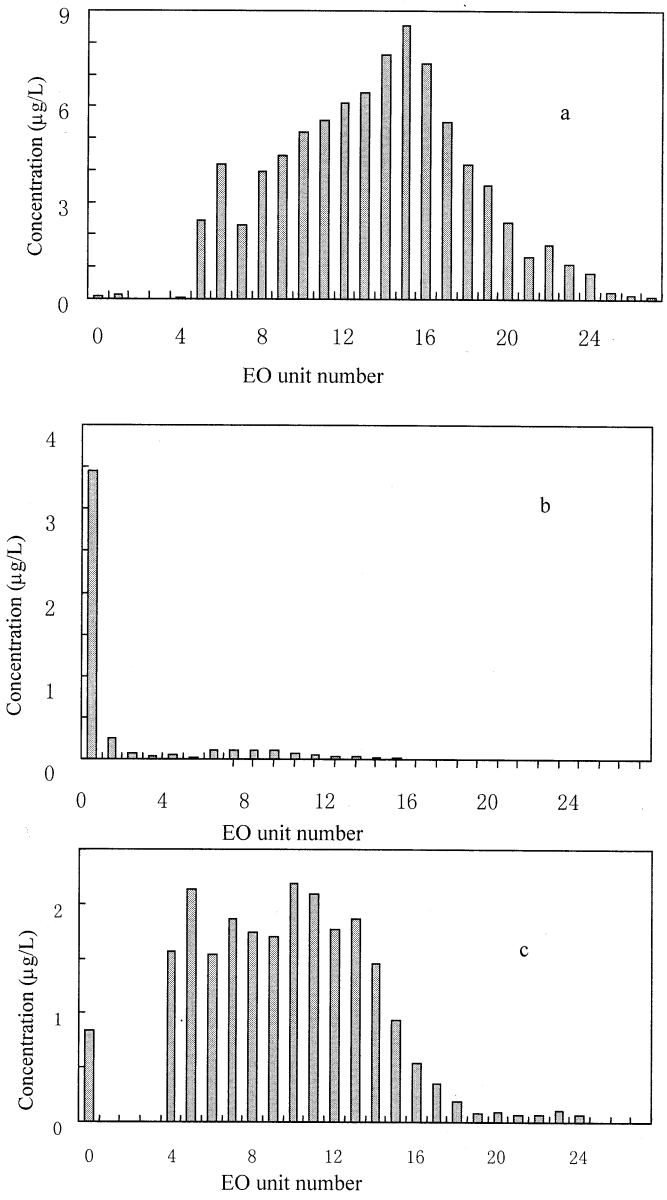

Fig. 2. Distribution of 4-nonylphenol and nonylphenol ethoxylates in river samples of site A. (a) April 2000; (b) July 2000; (c) December 2000.

Table 1. Concentrations of 4-NP and NPEOs in river water and corresponding drinking water (μg/L)

	April					July					December				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
4-NP (river water)	0.1	0.3	0.4	1.3	0.4	3.5	7.3	2.9	3.1	1.7	0.6	2.1	0.6	3.8	1.3
NPEOs(river water)	84.9	88.9	97.6	77.2	6.9	1.1	2.6	1.3	1.0	2.1	35.2	6.6	52.7	36.6	2.5
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
4-NP (drinking water)	ND*	0.05	0.01	ND	0.06	0.2	2.7	0.7	0.9	0.1	ND	0.2	0.01	0.02	0.02
NPEOs(drinking water)	0.3	0.2	0.1	0.2	0.3	0.1	0.3	ND	ND	ND	0.2	0.1	0.3	0.2	0.2

ND – not deteced, 4-NP, 4-nonylphenol; NPEOs, nonylphenol ethoxylates.

NPEOs in river water is consistent with that found in three main rivers in Tokyo, Japan (Maruyama *et al*. 2000).

NPEOs and 4-NP for each sampling site detected in the river samples are summarized in Table 1. In sites A to D, NPEOs, the prevailing species, in the samples in April were as high as 97.6 μg/L, much higher than those reported in other countries (Maruyama et al. 2000; Blackburn *et al*. 1995). 4-NP, however, became the dominating species in July, and the concentration level ranged from 1.55 to 7.33 μg/L.It is clear that water temperature was an important factor affecting the fate of NPEOs.

Site E was in the upper stream of the Jialingjiang River. From the fact that the NPEOs at site E in April and December were about one-tenth that of sample at site D, it is easy to speculate that the main pollution sources were located between sites E and D. Due to the low sewage treatment ratio (in Chongqing area, it is estimated to be no more than 10% at the time) (http://www.cqpa.gov.cn/lxryzl/3/info-20020611-2.htm), most of industrial wastewater was discharged into the rivers without biological treatment.

On the other hand, for the samples from the Changjiang River in April, the NPEOs and 4-NP at site A were 84.9 μg/L and 0.1 μg/L, respectively, which were similar to those at site B (88.9 μg/L and 0.30 μg/L, respectively). Moreover, in December, the NPEOs and 4-NP at site A were 35.2 μg/L and 0.6 μg/L, about fourfold of the concentration at site B with 6.7 μg/L NPEOs and 2.1 μg/L 4-NP. It is possible that the main sources were located upstream of site A.

As for the results in July, the NPEOs and 4-NP at site A were 1.1 μg/L and 3.5 μg/L, which was about half of that at site B (NPEOs, 2.6 μg/L; 4-NP, 7.3 μg/L). This phenomenon can be explained by the gradual biodegradation during transformation and discharging between A and B.

In addition, the highest concentrations of NPEOs in both April and December were found at site C, located at the convergence of the two rivers, which is probably due to the discharging of some industrial wastewater near this site where many workshops are distributed. The surfactants discharged into the two rivers seemed to be different. The highest individual NPEO concentration in the Changjiang River was attributed to NP15EO, while NP9EO and NP10EO predominated in the Jialingjiang River.

Concentration Levels of 4-NP and NPEOs in Drinking Water

Figure 3 shows the distribution of NPEOs in drinking water taken from distribution tanks at site A of the Changjiang River.

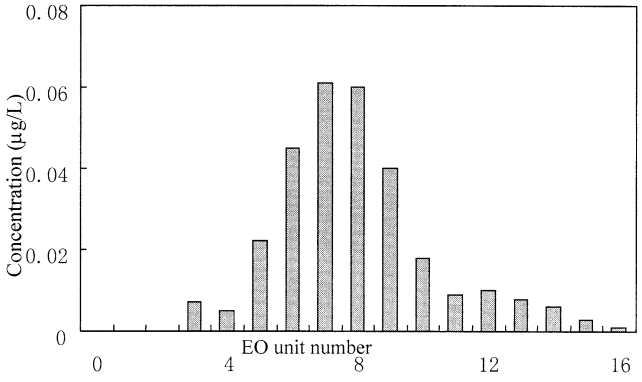

Fig. 3. Distribution of 4-nonylphenol and nonylphenol ethoxylates in the drinking water of site A taken in April 2000

Compared with those in raw water, the most abundant NPEOs species shifted from NP15EO to NP8EO, demonstrating that NPEOs with longer EO units are more easily removed by the water treatment process.

As described in the experimental section, the five sampling sites of the two rivers correspond to the water intakes of the five waterworks, which use the conventional process including coagulation with polychloride aluminum, sedimentation, sand filtration and chlorination. Table 1 lists the concentrations of 4-NP and NPEOs in all the drinking water samples. It is clear that NPEOs could be removed with an efficiency as high as 95% to 99% for samples in April and December. In spite of the high concentrations of NPEOs in some source water samples, the conventional water treatment process was efficient enough to remove NPEOs. The removal of NPEOs was perhaps the result of adsorption by coagulants.

The 4-NP removal rate, on the other hand, varied in a range from 62% to 94%, resulting in a considerably high residual 4-NP concentration in drinking water in July (0.1–2.7 μg/L). It seemed that adsorption only by the coagulant was not sufficient for 4-NP removal. It should be noted that a part of the removed 4-NP would be chloridized to form several halogenated byproducts, which may elicit antagonist action (Hu *et al*. 2002). Considering that the main drinking water sources in Chontqing Area are from the Jialingjiang River and the Changjiang River, advanced treatment processes such as activated carbon adsorption or ozonation (Paune *et al*. 1998) will be necessary to reduce the potential risk of 4-NP in drinking water.

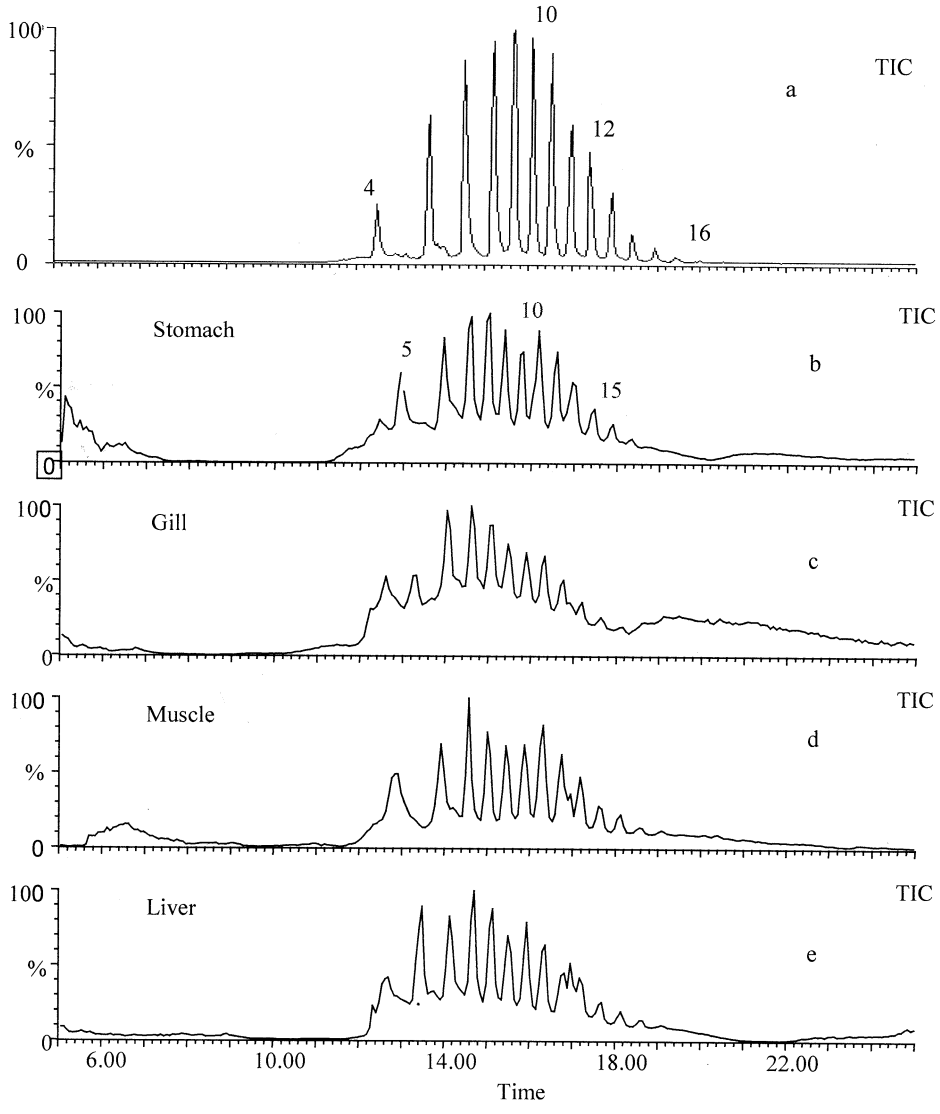

Fig. 4. The typical liquid chromatography–mass spectrometry chromatograms of nonylphenol ethoxylates in organs and muscle of *Leptobotia elongata*

Concentration Levels of 4-NP and NPEOs in Fish and Bioaccumulation

Considering the high residual concentration of 4-NP and NPEOs in river water, it is necessary to further investigate the residual levels in fish since this is another way that humans are exposed to 4-NP and NPEOs. Figure 4 shows the typical chromatograms of NPEOs in the organs and muscle of *Leptobotia elongata*. Similar NPEOs distribution patterns were found in all of the fish samples. NPEOs with EO chains of 6–8 showed the highest abundance, the profiles of which show little difference from that of a standard NPEO sample. This result may be associated with the low sewage treatment ratio (about 7%) (http://www.cqpa.gov.cn/lxryzl/3/info-20020611-2.htm) in the Chongqing area.

As for the distribution of 4-NP and NPEOs in organs and muscle, the highest concentration (20.2 μg/g) was found in liver, followed by those in the gill (2.1 μg/g) and in the stomach (2.2 μg/g); the lowest concentration was found in muscle (1.4 μg/g). Such a distribution of NPEOs in all organs was also found in other species. The concentrations of 4-NP in liver, stomach, gill, and muscle were 0.8 μg/g, 0.2, 0.1, and 0.1 μg/g, respectively.

Table 2 shows the analytical results of the fish samples. For *Rhinogobio typus*, the concentration of 4-NP ranged from 0.02 to 0.09 μg/g in muscles, 0.8 to 1.9 μg/g in livers, and 0.1 to 0.4 μg/g in the gills. The 4-NP concentrations in fish muscles were in the proper range compared with those reported by other researchers (from <0.003–0.008μg/g to <0.1–0.8 μg/g; Blackburn *et al*. 1999; Lye *et al*. 1999; Keith *et al*. 2001). However, the residual 4-NP in the liver (0.8–1.9 μg/g) obtained in this study was higher than the residual 4-NP found in the liver tissues of fish sampled from the U.K. at Tyne and Tees estuaries (Lye *et al*. 1999).

The residual NPEOs concentrations in livers, gills, and muscles were as high as 20.2 to 48.3, 2.1 to 5.8, and 0.4 to 1.4 μg/g, respectively. The concentration of 48.3 μg/g is the highest level ever reported (Rice *et al*. 2003; Tsuda *et al*. 2000; Keith *et al*. 2001; Lye *et al*. 1999; Ferrara *et al*. 2001; Kannan *et al*., 2003).

Table 2. Concentration of 4-NP and NPEOs in fish tissues taken in December ,2000(μg/g)

Type of sample (River)	Data	4-NP	NPEOs
Coreius Guichenoti muscle (Changjiang)	Dec.	0.02	0.8
Coreious Guichenoti gill		0.4	5.8
Coreius heterodon muscle (Changjaing)	Dec.	0.08	0.5
Coreius heterodon gill			
Leptobotia elongata muscle (Changjiang)	Dec.	0.09	1.3
Coreius heterodon liver		0.8	20.2
Coreius heterodon gill		0.1	2.1
Rhinogobio typus muscle *(Jialingjaing)*	Dec.	ND	0.5
Rhinogobio typu gill		0.1	4.7
Rhinogobio ventralis muscle*(Jialingjiang)*	Dec.	0.02	0.4
Rhinogobio ventralis liver		1.9	48.3
Rhinogobio ventralis gil		0.2	3.5
Rhinogobio ventralis stomach		0.2	2.2

ND – not deteced, 4-NP, 4-nonylphenol; NPEOs, nonylphenol ethoxylates.

The 4-NP and NPEOs concentration levels in the water samples near sites B and D were used to estimate the bioconcentration factor (BCF), a ratio between the concentration of a chemical in the tissues of an organism and the concentration the chemical in water. Although the value of BCF in our study is not exactly true because of the migration, it can be an indicator of water pollution. The BCF of 4-NP ranged from 1 to 25, 6 to 102, and 80 to 204 in muscles, gills, and livers respectively, showing that 4-NP tends to accumulate in liver tissues. These results of field study were consistent with those reported by Tsuda *et al.* (2000), where BCF for 4-NP was estimated in the range of 13–408. For NPEOs, the BCF is from 5 to 36, 40 to 157, and 57 to 5100 in muscles, gills, and livers, respectively, indicating that NPEOs are more easily bioconcentrated in fish than 4-NP. As we have determined, the sewage treatment ratio in Chongqing is very low (http://www.cqpa.gov.cn/lxryzl/3/info-20020611-2.htm), furthermore, there are no sewage treatment plants near the sampling sites because of the existence of the waterworks. Therefore, the levels detected in our study are higher than that found in other countries.

Potential Risk

As for human health implications, epidemiological studies are not available, and toxicological ones are limited. Therefore, the human health implications associated with these results are difficult to predict. A 90-day oral subchronic toxicity for rats indicated that 4-NP did not cause any effects at 50 mg/kg bw/day (Cunny *et al.* 1997). On the assumption that one person takes in 200 g river fish tissues and 2 L drinking water, the maximum of 4-NP was estimated to be 390 μg/person/day, or 65 μg/kg bw, which is much lower than that which can elicit subchronic toxicity on laboratory rat (Cunny *et al.* 1997). Although there is a low risk of 4-NP from the view of human consumption, more attention should be paid to ecological risk because the highest levels of 4-NP and NPEOs ever reported were found in *Rhinogobio ventralis* liver. It should be noted that 4-NP concentration near the threshold concentration (10 μg/L) that affects fish reproduction (Jobling *et al.* 1996) occurred in the Chanjing River.

Finally, the results obtained in this study filled existing gap in China, and provided useful information for related researchers and policy makers in the world.

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