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Nonylphenol ethoxylates and their metabolites in sewage treatment plants and rivers of Tianjin, China

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ABSTRACT

Nonylphenol polyethoxylates (NPnEO) and nonylphenol (NP) have provoked much environmental concern because of their weak estrogenic activities. We monitored NPnEO and their metabolites in rivers in Tianjin and in a sewage treatment plant of Tianjin monthly for 1 year. The total concentrations of NPnEO and NP in influent, up to 47.2 μg L^{-1} in August, were higher in summer than in other seasons. During the 12 months survey, NP was accumulated in most effluent samples with a mean value of 2.92 μg L^{-1}. The average concentrations of nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO) and nonylphenol triethoxylate (NP3EO) in effluents were 1.26, 1.53 and 1.06 μg L^{-1}, which corresponds to percent removals of 75%, 60% and 62%, respectively. In rivers of Tianjin, NP2EO and nonylphenoxyethoxy acetic acid (NP2EC) exhibited the highest concentrations in the surface water, up to 1.38 and 9.59 μg L^{-1}, respectively. The pollution of nonylphenolic substances in sediments of Haihe River belongs to moderate or severe level in the world, with the total concentration between 4.1 and 9.9 μg g^{-1}, dry weight.

1. Introduction

Alkylphenol polyethoxylates (APnEO) are one of the most widely used classes of surfactants, which have been used as industrial and domestic detergents, herbicides, paints, and cosmetics (Ahel et al., 1994). Among APnEO, nonylphenol polyethoxylates (NPnEO) are the most commonly used, accounting for more than 80% of the world market (Renner, 1997). Approximately 700 kt of NPnEO are produced annually worldwide (Jonkers et al., 2005) with 50 kt in China. About 60% of the surfactants finally enter natural water environments via various pathways, such as municipal or industrial wastewater discharges, and sewage treatment plant (STP) effluents (Ying et al., 2002). Once NPnEO are present in water bodies, they are biodegraded by removal of ethoxyl groups (Ahel et al., 1994), yielding relative stable small metabolites, such as nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenoxy acetic acid (NP1EC) and nonylphenoxyethoxy acetic acid (NP2EC) (La Guardia et al., 2001; Ying, 2006; Loos et al., 2007). Unfortunately, these small metabolites of NPnEO are more persistent and toxic than the parent compounds (Shang et al., 1999; Berryman et al., 2004). Furthermore, endocrine disrupting activities to fish, bird and mammal cells in vitro were also observed (Jobling and Sumpter, 1993; Ying et al., 2002).

Tianjin is the third biggest city in China with an area of 12 000 km^2 and a population of 10 million. The main drinking water resources of Tianjin are composed of Luanhe River, Yellow River, which are both channeled into Tianjin from Hebei Province, and Haihe River as a potential drinking water resource. Haihe River is the most polluted river among the seven largest water systems in China. Jin et al. (2004) have reported that NP concentrations ranged from 0.11 to 0.55 μg L^{-1} in the surface water of Haihe River. However, a comprehensive investigation on pollution of NPnEO and their metabolites in drinking water resources of Tianjin is still necessary. Moreover, to our knowledge, no studies focused on the occurrence and distribution of NPnEO in STPs in Tianjin, which might be the major sources of NPnEO in rivers.

The purpose of the present study was to evaluate the concentration levels of NPnEO and their metabolites in STPs and drinking water sources of Tianjin. The information adds new data to the global database, and provides valuable information for pollution control in this area.

2. Materials and methods

2.1. Chemicals and reagents

NP, NP1EC and NP2EC (technical grade) were purchased from Tokyo Chemical Synthesis Ind. Co., Japan. NPnEO (n = 1–15, technical grade) mixture was product of Liaoyang Chemical Plant, China. Isopropanol, n-hexane, methanol and water were all of HPLC

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grade, and dichloromethane (DCM), ethyl ether and anhydrous sodium sulfate were of analytical grade. Florisil (60–100 mesh size; Tianjin Jiangtian Chemical Reagent Corp., China) was activated at 130 °C for 16 h before use. Waters Oasis™ HLB cartridges (Waters Company, USA) were used as solid phase extraction (SPE) material.

2.2. Study area and sample collection

Water samples were collected from the influent and effluent of Tanggu STP in the time span from February 2004 to January 2005. The sampling surveys were carried out at intervals of 1 month. Water samples from the influent and effluent from Jizhuangzi STP and Dongjiao STP were collected in March 2005.

Twenty sampling sites were selected in three rivers of Tianjin (Fig. 1). Four sites (Y1–Y4) were located in the Yellow River, seven sites (L1–L7) were along the Luanhe River, and nine sites (H1–H9) were located in the Haihe River. In March 2005, surface water samples (at a depth of approximately 0.5 m) were collected from all sampling sites, and surface sediment (0–10 cm) samples were collected from Haihe River (H1–H9) using a stainless steel grab sampler and placed in glass bottles with Teflon lined caps.

The water samples were treated immediately after sampling or stored at 4 °C after adding 1% (v/v) formaldehyde. The sediment samples were transported to the laboratory at 0 °C, dried in a freeze-drier (ALPHR 1-2 LD, Martin Christ Gefriertrocknungsanlagen GmbH, Germany), ground and stored at −20 °C before analysis.

2.3. Chemical analysis

One liter water sample was filtered through 0.45 μm microporous filter membrane. The filtered water was immediately acidified to pH = 2.5 with HCl and extracted with SPE method using Oasis HLB cartridges. Conditions of SPE were as follows: washed with 2.0 mL methanol/DCM (50/50, v/v), activated with 1.0 mL methanol, and then equilibrated with 1.0 mL water. The acidified filtered water was loaded through the cartridge at a flow rate about 10 mL min^{-1}. The cartridge was then cleaned up with 1.0 mL methanol/water (5/95, v/v) and eluted with 1 mL methanol and 1 mL methanol/DCM (50/50, v/v).

Five gram 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 °C in water bath by a rotary evaporator (RE-52AA, Shanghai Ya-Rong Biochemical Instrument Factory, China), and then purified by passing through a 25 × 1.0 cm i.d. 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, eluted with 80 mL of ethyl ether and hexane (1:9, v/v). The elute was concentrated to almost dryness under a gentle N_2 stream, and 0.5 mL of *n*-hexane was then added to redissolve the residue.

Waters 1525 high performance liquid chromatography (HPLC), with a 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 × 10 μm, Waters Corp., Ireland) was used for the separation of NP and NPnEO by normal-phase HPLC. 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 mobile phase for NP and NPnEO analysis. Gradient elution was carried out with a linear program from 95% A and 5% B to 30% A and 70% B in 35 min, then to 95% A and 5% B in 55 min with a flow rate of 1.0 mL min^{-1}. Excitation and emission wavelengths of the fluorescence detector were 233 and 302 nm, respectively. Injection volume was 20 μL.

A Waters W23041T005 RP_{18} column (Symmetry Shield™ 3.9 mm i.d. × 150 mm × 5 μm, Waters Corp., Ireland) was utilized for analysis of NP1-2EC, which mobile phase was made up of pure methanol (A) and methanol/water (1/3, v/v, B) containing 2 mM ammonium acetate. A linear program from 10% A and 90% B to 100% A and 0% B in 40 min was carried out with a flow rate of 0.25 mL min^{-1}. Excitation and emission wavelengths of the fluorescence detector were 225 and 295 nm, respectively. Injection volume was 20 μL (Wang et al., 2006; Hou and Sun, 2007).

All water samples were analyzed for DOC using a total organic carbon analyzer (TOC-VCPH; Shimadzu, Japan). A Dionex ICS-1000 ion chromatography (IC), with a Dionex IonPac AS14 detector was utilized for the determination of chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) anions in water samples. Mixtures of sodium carbonate (3.5 mM) and sodium bicarbonate (1.0 mM) were used as mobile phase. The flow rate was 1.2 mL min^{-1} and injection volume was 10 μL.

2.4. Quality assurance and quality control

Procedural blanks were analyzed concurrently with the water and sediment samples. The water blanks consisted of 1000 mL double distilled water, and were extracted in the same manner as the water 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. NPnEO and NPmEC were not detected in the sediment and water blanks. Their limits of detection (LOD) were 3–6 ng g^{-1} for sediment and 0.015–0.030 μg L^{-1} for water. Water and sediment samples were spiked with specific amount of NP, NPnEO (n = 1–15), NP1EC and NP2EC to determine the recovery. The average recoveries and the relative standard deviation (RSD) in sediment and water were 93 ± 4% and 87 ± 5.1% (NP), 83 ± 6% – 96 ± 4% and 83 ± 8% – 102 ± 2.0% (NPnEO, n = 1–15), 74 ± 3% and 69.5 ± 4.0% (NP1EC), 72 ± 5% and 74.5 ± 3.7% (NP2EC), respectively.

3. Results and discussion

3.1. Occurrence of NPnEO and NP in STPs

Tanggu STP, located between H7 and H8, treats both domestic and industrial wastewater. The analytical results for Tanggu STP during February 2004–January 2005 are presented in Table S1 (supplementary material) and Fig. 2. NP and NP1-6EO were detected in all influent samples except in March, 2004. The total concentrations of NP and NP1-12EO in influents ranged from 14.0 to 47.2 μg L^{-1}. The highest concentration was found in August and high levels were also measured in June, July and September, which might be due to higher uses in summer. Among the analogs, NP1EO and NP2EO had the highest concentrations in the STP influents, showing mean values of 4.96 and 4.72 μg L^{-1}, respectively.

In the effluent, the concentrations of NPnEO (Fig. 2) decreased obviously compared to the influent. The total concentrations of NP and NP1-12EO ranged between 4.73 and 21.4 μg L^{-1}. By comparing the influent–effluent concentrations, we calculated the NPnEO removal rate or degradation by the STPs. As shown in Table S2 (supplementary material), the long chain NPnEO (n > 6) experienced relatively high and stable removal rates ranging from 82.6 to >99% on average; however, the removal rate of short chain NPnEO (n < 6) was lower than those of long chain NPnEO. Moreover, it is interesting to find that NP5EO has the lowest removal rate. This could be mainly attributed to the contribution from the incomplete degradation of long chain NPnEO. NP, as a stable degradation product, was accumulated in all effluent samples, with NP values lying between 1.32 and 5.22 μg L^{-1}, except in April 2004, which had the highest concentrations among the effluents analyzed. Concentrations of NP1EO, NP2EO and nonylphenol triethoxylate (NP3EO) in