Fate of nonylphenol polyethoxylates and their metabolites in four Beijing wastewater treatment plants

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ABSTRACT

Four Beijing wastewater treatment plants (WWTPs) were selected to investigate behaviours of nonylphenol polyethoxylates and their metabolites in different wastewater treatment processes. The results showed that the total concentrations of nonylphenolic compounds in the influents of the four WWTPs ranged from 0.115 to 0.347 $\mu\text{mol/L}$, as well as their removal efficiencies ranging from 75.7% to 90.8%. Both influent concentrations and removal efficiencies of nonylphenol polyethoxylates were correlated to seasons as follows: higher in the summer than in the winter, and influent concentrations were lower during the rain weather. The analysis revealed that 21.8–47.6% of nonylphenol polyethoxylates and their metabolites entering WWTPs were released via effluents and excess sludge, leaving a great part of them for biodegradation. Nonylphenol and short-chain nonylphenol polyethoxylates were disposed to the environment mainly via sewage sludge, while carboxylated nonylphenol polyethoxylates were the most abundant group of nonylphenol polyethoxylates in effluents.

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1. Introduction

Nonylphenol polyethoxylates (NPnEOs, n : number of ethoxy units) are an important group of non-ionic surfactants, which are manufactured and utilized in many households, institutions and industries. The worldwide production of alkylphenol ethoxylates (APEOs) has been estimated to be 500,000 tons per year (Fujita and Reinhard, 1997), of which NPnEOs account for approximately 80%. Since 1995, the consumption of NPnEOs in China has increased steadily, and its estimated total consumption is 60,000 tons per year in recent years (Zhang et al., 2007). Previous literatures have suggested that NPnEOs consist in municipal wastewater. Throughout the wastewater treatment, due to biodegradation, NPnEOs undergo a rapid transformation into short-chain NPEOs such as nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO), nonylphenol (NP), and carboxylated derivatives including carboxylated NPnEOs (NPECs) and dicarboxylated NPnEOs (CAPECs) (Soares et al., 2008). NP and short-chain NPnEOs ($n=1,2$) are lipophilic compared with the long-chain ethoxylates, and have been reported to cause a number of estrogenic responses on aquatic organisms, thus they have been classified as endocrine disruptors (EDCs) (Scrimshaw and Lester, 2003). Moreover, NP1EC and NP2EC are also proved to have the estrogenic properties (Harries et al., 1996). Therefore, the exposure of these persistent and toxic biodegradation products with the release of effluent and excess sludge during wastewater treatment plants (WWTPs) has been paid more and more attention.

So far, the fate and occurrence of NPnEOs and their metabolites in WWTPs have been well documented through several studies around the world (Jobling and Sumpter, 1993; Korner et al., 2000; Soares et al., 2008; Stasinakis et al., 2008). However, most of the reports limited the number of analytes to NP and NPnEOs, while only a few reports included NPECs and CAPECs (Ahel et al., 1994; Corcia et al., 2000; Fujita et al., 2000; Loyo-Rosales et al., 2007). Especially in China, there has been no data for NPECs in WWTPs up to date. Moreover, despite the existence of several studies investigating the presence of nonylphenolic compounds in WWTPs, most of them focused exclusively on concentrations in influents and effluents (Ma et al., 2002; Shao et al., 2003; Hao, 2007), and then removal efficiencies were obtained. Only a few reports have made mass balance of nonylphenolic compounds in WWTPs to obtain the output pathways of nonylphenolic compounds (Ahel et al., 1994; Bruno et al., 2002; Loyo-Rosales et al., 2007). Moreover, the contributions of the pathways were rarely determined probably due to the difficulty in detecting all the nonylphenolic compounds in wastewater and sludge samples and in getting accurate operational parameters of WWTPs. In addition, the fate of organic compounds during wastewater treatment processes is controlled by physical, chemical and biological processes of wastewater treatment (Scrimshaw and Lester, 2003). NP, short-chain NPnEOs, long-chain NPnEOs and NPECs may display different output modes because of their different physical and chemical properties. However, much less reports are available for the output pathway of each kind of NPnEOs metabolites.

In this study, a comprehensive study on the occurrence, transformation and elimination of NPnEOs and their metabolites was carried out in four full-scale WWTPs of Beijing, China. The impacts of weather on the behaviour of NPnEOs and related compounds were also investigated.

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These results would be helpful to assess and control removal of NPnEOs and their metabolites, in order to improve the work efficacy of WWTPs in China.

2. Materials and methods

2.1. Standard solutions and reagents

4-NP (technical grade), a mixture of compounds with branched side chains, was obtained from TCI Chemicals (Tokyo, Japan). Pure NP1EO, pure NP2EO and NPECs mixture standards (with EO chain lengths from 0 to 9, corresponding from NP1EC to NP10EC) were purchased from Hayashi Pure Chemicals (Osaka, Japan). A non-ionic surfactant, Igepal CO630 (a commercial nonylphenol polyethoxylate mixture with an average of 9EO units), was obtained from Sigma-Aldrich (Gillingham, UK). Standard stock solutions were prepared in methanol. Sodium acetate (p.a) was purchased from Beijing Chemical Reagents Company. Dichloromethane, methanol and hexane were HPLC grade (Fisher Chemical Co., USA). Ultra pure water was prepared using a CUPW-10N ultrapure water system (Liyuan, China) at a conductivity of $18.3 \Omega \cdot \text{cm}^{-1}$. Silica-based bonded C18 (Sep-Pak, 6 cc, 500 mg) and poly (divinylbenzene-co-*N*-vinylpyrrolidone) (Oasis HLB, 6 cc, 500 mg) cartridges were supplied by Waters (Milford, MA, USA).

2.2. WWTPs surveyed and sampling

Four full-scale WWTPs in Beijing were studied from June to December in 2007 and July in 2008. Information on the individual plant and their operational parameters are summarized in Table 1. Plant 1, plant 2 and plant 4 receive both industrial and domestic wastewaters, while plant 3 treats only domestic wastewater. The treatment processes of the four WWTPs are different from each other, being anaerobic–anoxic–oxic (A^2O), anaerobic–oxic (AO), anaerobic–anoxic–oxic (A^2O) combined with biofilm and oxidation ditches, respectively. Twenty-four-hour composite samples of influents were taken in each of WWTPs, while grab effluents samples and sludge samples were collected from each processing unit of the WWTPs. All sampling campaigns were conducted during the dry weather, except for two sampling events in the rain weather, on July 11th and 14th in 2008, respectively. Wastewater and sewage sludge samples were collected in pre-cleaned amber glass bottles. Soon after the sampling, wastewater samples were added with formaldehyde (1%, v/v), then filtered and stored in the dark at 4 °C. The filters were air-dried and weighed to calculate suspended solids, and extracted to evaluate NPnEOs and relative compounds. Their extraction was performed within 48 h of their arrival. Sludge samples were frozen at –20 °C before freeze-dried (ALPHA 1-2LD PLUS, Christ, Germany). After lyophilization, the sludge was homogenized and stored frozen, wrapped in aluminum foil, to avoid any contact with plastic material.

2.3. Extraction and analysis

For wastewater, a volume of 500 ml of wastewater sample was filtered through a pre-ashed (4 h, 450 °C) glass fiber filter (GF/F, pore size 0.7 μm , Whatman, Brentford, Middlesex, UK) and acidified with

concentrated HCl (37%, GR). A HLB cartridge was conditioned sequentially with 5 ml CH_2Cl_2 , 5 ml CH_3OH , and 5 ml water. The acidified water (pH=3) was passed through the HLB cartridges at 5–10 ml/min, and the residual water was removed by passing a gentle nitrogen stream through the cartridges for about 30 min. A total of 10 ml of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (80:20, v/v) was used as eluent, and passed through the sorbent beds at a rate of 2 ml/min to desorb NPnEOs. The eluent was dried under a gentle nitrogen stream followed by adding 0.05 ml 4-n-NP (10 mg/L in hexane) and 100 μL BSTFA + TMCS reagents, then reconstituted with 1 ml hexane, 0.4 ml of which was separated to analyze NP and NPnEOs ($n=1,2$) with gas chromatograph–mass spectrometer (GC–MS). For the quantitative analysis, a gas chromatograph 6890 Series connected to a MSD 5975i was used (Agilent, USA). The carrier gas was helium and maintained at a constant flow rate of 0.9 ml·min^{–1}. A sample volume of 1 μL was injected in splitless mode at an inlet temperature of 300 °C. The column temperature was programmed as follows: at 50 °C for 1 min, from 50 °C to 200 °C at a rate of 20 °C/min, at 200 °C for 2 min, from 200 °C to 235 °C at a rate of 5 °C/min, at 235 °C for 5 min, from 235 °C to 280 °C at a rate of 25 °C/min, and at 280 °C for 5 min. The EI conditions were: ionization energy, 70 eV; electron multiplier voltage, 1.45 kV. Quantitative analysis was carried out using selected ion monitoring (SIM) mode. For each compound, the most abundant ions were selected from its spectrum. The chosen ions for SIM were 179 for 4-n-NP; 221,179,193 for NP; 251,265 for NP1EO; and 295,309 for NP2EO. The remaining 0.6 ml hexane was dried and reconstituted with 1 ml $\text{CH}_3\text{OH}/\text{water}$ (1:1, v/v) for liquid chromatography–electrospray ionization–mass spectrometry (LC–ESI–MS) analysis, in order to detect NPnEOs ($n \geq 3$) and NPECs (Zhang et al., 2007). Analysis were performed on an Alliance 2690 HPLC (Waters Corporation, USA) equipped with a C18 analytical column (2.1 mm in ID $\times$ 150 mm in length, 3 μm Waters Symmetry Shield, USA) and ZQ4000 MSD (Waters Corporation, USA). The column oven was at 40 °C, and the injection volume was 20 μL . The mobile phases consisted of water containing 0.1 mmol/L sodium acetate (A) and methanol (B). The flow was kept at 0.2 ml/min for 5 min with 30% methanol, then the methanol was linearly increased to 85% in 7 min and held for 9 min, afterwards changed to 97% immediately and held for 6 min, finally brought back to 30% and held for 7 min to the next injection. The capillary voltage was 3.5 kV; the cone voltage was 30 V; source temperature and desolvation gas temperature were set to 100 °C and 300 °C; the flow rate of the desolvation gas and cone gas were 250 L/h and 60 L/h respectively. The full scan mass ranged from 200 to 1500 Da with a scan time of 1 s.

For sludge samples and solids on the filter membranes, target compounds were extracted with a solvent mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (70:30, v/v). One gram of lyophilized and homogenized sludge sample or a piece of lyophilized filter membrane with solids on it was sonicated for 10 min with 15 ml of the solvent mixture. The extract was separated by centrifugation at 4000 rpm for 10 min, and the procedure was repeated three times. The extracts were combined, concentrated to an approximate volume of 1 ml using a rotary vacuum evaporator at 35 °C, and redissolved in 500 ml of water. Subsequent cleanup of extracts was performed by SPE as described above, except

Table 1
Wastewater treatment plant characteristics and sampling events.

	Plant 1	Plant 2	Plant 3	Plant 4
Location in Beijing	North–west, 40°02'N, 116°21'E	East, 39°53'N, 116°31'E	East–south, 39°51'N, 116°26'E	South, 39°43'N, 116°23'E
Capacity ($\times 10^3 \text{ m}^3/\text{day}$)	450	750	40	54
Wastewater source	Domestic, industrial	Domestic, industrial	Domestic	Domestic, industrial
Treatment process	A^2O	AO	A^2O combined with biofilm	Oxidation ditches
Sludge treatment	Centrifugal dewatering	Anaerobic digestion	Dewatering by filter press	Centrifugal dewatering
HRT, h	15	6–9	9.6	9
SRT, d	12–15	20	10	15
Sampling events	June 2007, July 2007, September 2007, July 2008	September 2007, December 2007	October 2007, December 2007	October 2007, July 2008

Table 2

Method detection limits (MDLs), mean recoveries and relative standard deviations (RSDs) of nonylphenolic compounds in wastewater and sludge samples, obtained using GC–MS and LC–ESI–MS analysis.

	Wastewater samples		Sludge samples	
	MDL(ng/L)	Recovery(%) ± RSD(%)	MDL(μg/kg)	Recovery(%) ± RSD(%)
NP	2.5	87 ± 5.5	6.5	80 ± 7.4
NP1EO	2.5	88 ± 5.6	7.5	85 ± 8.6
NP2EO	3.0	83 ± 3.2	11.0	78 ± 6.7
NPEOs (<i>n</i> = 3–15)	0.02	81 ± 5.8	0.07	79 ± 5.6
NPECs	0.1	88 ± 6.4	0.3	78 ± 4.6

that the HLB cartridge was changed to C18 cartridge. The method detection limits (MDLs) and the recoveries of the nonylphenolic compounds, as well as relative standard deviations (RSDs) obtained using the above analytical method were listed in Table 2.

3. Results and discussion

3.1. NPnEOs and their metabolites in the influents and effluents of the WWTPs

Results of the analyses of NPnEOs and their metabolites in wastewater samples taken from the four WWTPs in Beijing are summarized in Table 3.

Based on their characteristic behaviour during wastewater treatment, NPnEOs and their metabolites were divided into four groups: NP, NPnEOs (*n* = 1,2), NPnEOs (*n* ≥ 3) and NPECs. Each oligomer of NPnEOs from NP3EO to NP15EO and each oligomer of NPnECs from NP1EC to NP10EC were detected respectively, and the presented levels of NPnEOs (*n* ≥ 3) and NPECs in the study were the sums of the concentrations of these oligomers. It is clear that the total concentrations of nonylphenolic compounds (NP-c) in the dry weather is related to industrial and domestic wastewater content in the WWTPs influents, i. e., 0.115 to 0.183 μmol/L of NP-c in the WWTPs receiving both industrial and domestic wastewaters, and 0.347 μmol/L of NP-c in the WWTP receiving only domestic wastewater. The concentrations of nonylphenolic compounds detected in this study fell into the range reported in other literatures (Ma et al., 2002; Planas et al., 2002; Hou and Sun, 2006; Stasinakis et al., 2008), but were at low level compared to those observed in the European countries, such as Switzerland (2.42–4.05 μmol/L) (Ahel et al., 1994) and United States (425–894 μg/L for NP0–16EO) (Loyo-Rosales et al., 2007), indicating that the contamination in Beijing seemed less heavy than abroad, probably due to less consumption of NPnEOs surfactants in Beijing.

The relative abundance of the four groups of different NPnEOs relative compounds in the sewage influents of the four WWTPs is presented in Fig. 1a. The contribution of each nonylphenolic compound group in a WWTP is the average of the results obtained during several sampling events. NPnEOs (*n* ≥ 3) contributed 5.3–31.7% to the total in the influents, accordingly, the sum of NP, NPnEOs (*n* = 1,2) and NPECs contributed to

Table 3

Occurrence (dissolved + particulate matter) and elimination of NP-c in four WWTPs of Beijing, China (ND, not detected).

Sampling time	T(°C)	Samples	Concentration(μmol/L)				Sum	Removal (%)
			NP	NPnEOs (<i>n</i> = 1,2)	NPEOs (<i>n</i> ≥ 3)	NPECs		
Plant 1								
June, 14th	25.7	Inf.	0.029	0.067	0.009	0.021	0.126	88.0
		Eff.	ND	0.004	0.001	0.010	0.015	
July, 8th	23.8	Inf.	0.035	0.044	0.005	0.031	0.115	75.7
		Eff.	0.001	0.008	0.001	0.018	0.028	
July, 24th	25.3	Inf.	0.032	0.053	0.007	0.038	0.130	80.8
		Eff.	0.002	0.002	0.001	0.020	0.025	
Sep, 11th	22.9	Inf.	0.042	0.052	0.008	0.043	0.145	81.4
		Eff.	0.002	0.001	0.001	0.023	0.027	
July, 11th	20.5	Inf.	0.019	0.032	0.004	0.021	0.076	82.9
		Eff.	0.001	0.001	0.001	0.010	0.013	
July, 14th ^a	24.1	Inf.	0.021	0.036	0.005	0.014	0.076	85.5
		Eff.	0.002	0.001	0.001	0.007	0.011	
July, 18th ^a	25.3	Inf.	0.040	0.055	0.008	0.018	0.121	86.0
		Eff.	0.002	0.004	0.001	0.010	0.017	
Average ± S.D. (in dry weather)		Inf.	0.036 ± 0.005	0.054 ± 0.008	0.007 ± 0.001	0.030 ± 0.011	0.127 ± 0.011	82.4 ± 4.8
		Eff.	0.001 ± 0.001	0.004 ± 0.002	0.001 ± 0.000	0.016 ± 0.005	0.022 ± 0.005	
Plant 2								
Sep, 27th	20.7	Inf.	0.037	0.064	0.016	0.032	0.149	89.9
		Eff.	0.001	0.001	0.001	0.012	0.015	
Dec, 17th	13.8	Inf.	0.029	0.071	0.013	0.023	0.136	89.7
		Eff.	0.001	0.002	0.002	0.009	0.014	
Average ± S.D.		Inf.	0.033 ± 0.005	0.067 ± 0.006	0.014 ± 0.002	0.028 ± 0.007	0.142 ± 0.008	89.8 ± 1.4
		Eff.	0.001 ± 0.000	0.001 ± 0.001	0.002 ± 0.001	0.010 ± 0.002	0.014 ± 0.001	
Plant 3								
Oct, 26th	20	Inf.	0.038	0.067	0.110	0.132	0.347	90.8
		Eff.	ND	ND	0.001	0.031	0.032	
Dec, 17th	14.8	Inf.	0.085	0.106	0.016	0.060	0.267	90.3
		Eff.	ND	ND	0.002	0.024	0.026	
Average ± S.D.		Inf.	0.062 ± 0.033	0.086 ± 0.027	0.063 ± 0.067	0.096 ± 0.051	0.308 ± 0.057	90.6 ± 3.5
		Eff.	ND	ND	0.002 ± 0.001	0.028 ± 0.005	0.030 ± 0.004	
Plant 4								
Oct, 26th	18.7	Inf.	0.034	0.036	0.028	0.085	0.183	88.0
		Eff.	ND	ND	ND	0.022	0.022	
July, 16th ^a	23.0	Inf.	0.030	0.028	0.034	0.080	0.172	89.5
		Eff.	ND	ND	ND	0.018	0.018	
Average ± S.D.		Inf.	0.032 ± 0.003	0.032 ± 0.005	0.031 ± 0.004	0.083 ± 0.004	0.178 ± 0.008	88.8 ± 1.1
		Eff.	ND	ND	ND	0.020 ± 0.003	0.021 ± 0.003	

^a The samplings times were in 2008, while others in 2007.

Fig. 1. Relative abundance of NPnEOs and their metabolites in sewage influents (a) and effluents (b) of the four WWTPs.

68.3–94.7% of the totals. These results were inconsistent with those of other countries, in which the group of long-chain NPnEOs was the most abundant group in the influent (82.4%) (Ahel et al., 1994), but were accordant with the other results obtained in China (Shao et al., 2003), which reported that NPnEOs ($n \geq 3$) was only one third of the total nonylphenolic compounds in the influents. The difference between China and other countries might be due to the relatively longer sewers entering WWTPs in China, so a large amount of long-chain NPnEOs were already transformed into the metabolites before introduced to WWTPs, resulting in the lower contribution than other countries. Distributions of nonylphenolic compounds between aqueous phase and solid phase in the influent were different. Taking the influent in one sampling event for plant 2 for example, Fig. 2 shows the percentages that dissolved portion and adsorbed portion occupied for each oligomer of nonylphenolic compounds. It can be seen that the adsorbed portion decreased as the EO chain length increased, and NPnECs occupied the smallest percentage. It is already known that the octanol–water partition coefficients $\log K_{ow}$ values for NP, NP1EO, NP2EO and NP3EO are 4.48, 4.17, 4.21 and 4.20, respectively (Ahel and Giger, 1993), and decreases as the EO chain length increases. Therefore, this finding supported that with the EO chain length increasing,

the NPnEO oligomers become more hydrophilic. In addition, the removals of nonylphenolic compounds in the dry weather were equally comparable across the four WWTPs, ranging from 75.7% to 90.8%, reflecting that good elimination of nonylphenolic compounds in wastewater could be achieved during existing wastewater treatment processes (Table 3).

Regarding the effluents of WWTPs, NPnECs were as expected the most abundant group (Fig. 1b), indicating NPnECs were the main metabolites of NPnEOs during biological degradation processes (Ahel et al., 1994; Loyo-Rosales et al., 2007).

3.2. Impact of weather on the occurrence and elimination of NPnEOs and their metabolites

For plant 2 and plant 3, sampling events occurred in September, October and December 2007, in order to study the impact of ambient temperature on the occurrence and elimination of NPnEOs and their metabolites in the WWTPs. As mentioned by a report (Loyo-Rosales et al., 2007), samples were considered as “the summer” if water temperature was above 20 °C and as “the winter” if it was below 15 °C. The total concentrations of nonylphenolic compounds in the influents and removal of NPnEOs ($n \geq 3$) in the summer and the winter for plant 2 and plant 3 were illustrated in Fig. 3. These results showed that the influent concentrations of both WWTPs were a little higher in the summer than in the winter. This phenomenon was probably due to more washing events and larger NPnEOs surfactants consumption in the summer. Correspondingly, there was a similar seasonal effect on the removal of NPnEOs ($n \geq 3$), in which higher NPnEOs ($n \geq 3$) removals occurred in the summer for the both plants. The other three groups of nonylphenolic compounds including NP, NPnEOs ($n = 1,2$) and NPnECs were not only biodegraded but also produced during wastewater treatment process, whereas NPnEOs ($n \geq 3$) were only biodegraded, so the removal of NPnEOs ($n \geq 3$) could reflect the extent of biodegradation. Obviously, high ambient temperature is helpful for higher biodegradation of the long-chain NPnEOs in both plants.

In previous studies, wastewater samples were generally obtained in the dry weather, and few studies have addressed the behaviour of nonylphenolic compounds in WWTPs in the rain weather. On July 11th and 14th in 2008, when Beijing was during the rainy season and the two days before which were continuously rainy, sampling events were conducted from plant 1, in order to discuss whether the rain weather had any effect on the influent concentrations and removal of nonylphenolic compounds. As shown in Fig. 4, June 14th, July 8th, July 24th, and September 11th in 2007 and July 18th in 2008 were sunny during the dry weather, while July 11th and 14th in 2008 were rainy. It can be seen that the total concentration of nonylphenolic compounds in the influents were remarkably lower in the rainy days approximately 60% of those in the dry weather. The difference was also observed in terms of COD in the influents. Compared to the dry weather, COD of the influents decreased 10–29% in the rain weather. It

Fig. 2. Distributions of nonylphenolic compounds in aqueous and solid phase of the influent in plant 2.

Fig. 3. The total influent concentrations of NP-c and removals of long-chain NPnEOs in the summer and the winter for plant 2 and plant 3.

was rainy everyday from July 9th to July 14th, and the input flow of plant 1 was about 500×10^3 – 600×10^3 m³/day during those days (data supplied by plant 1), which was about one third time larger than that in the dry weather, due to that the sewerage system that served plant 1 was not closed. Therefore, the dilution caused by the rainwater led to the lower levels of COD and nonylphenolic compounds in the influents. However, no remarkable differences were found in removal rates of both COD and nonylphenolic compounds between the dry weather and the rain weather (data not shown), indicating that rainfall had little impact on the removal efficiencies of nonylphenolic compounds and COD in the WWTP. This may be a compositive function caused by rainwater dilution, microorganisms and long hydraulic residence time (HRT) of the wastewater treatment system.

3.3. Output pathways of NPnEOs and their metabolites in WWTPs

In previous studies, the elimination of NPnEOs and their metabolites during wastewater treatment process was generally expressed by the ratios of nonylphenolic compounds concentrations in the effluent to those in the influent. The eliminated nonylphenolic compounds were perhaps not completely degraded, leaving a considerable amount being absorbed into sludge flocs due to their affinity to solids (Loyo-Rosales et al., 2007; Stasinakis et al., 2008; Pothitou and Voutsas, 2008). In this study, not only concentrations of nonylphenolic compounds in wastewater samples, but also those in sludge samples were determined, then mass balance of nonylphenolic compounds in the whole wastewater treatment processes can be obtained taking related WWTPs operational parameters into consideration (Fig. 5), and output pathways of NPnEOs and their metabolites in WWTPs can be summarized. Flow chart for a representative WWTP is given in Fig. 5, and various flow rates were introduced respectively for the four plants, in order to obtain mass balances of the total nonylphenolic compounds

in each of the four plants. The concentrations in wastewater and excess sludge samples introduced to get mass balances were the average values of the several investigation results in dry weather.

The nonylphenolic compounds removal in the grit chamber was first considered. Taking plant 1 as an example, the concentration of NP adsorbed to grits was 0.029 mmol/kg. Taking sand discharged amount into account, NP release via sand discharging could be calculated, being 0.3 mmol per day, accounting for 0.004% of NP input to the WWTP. The portion was too small to be considered, and other NPnEOs metabolites eliminations via sand discharge were also ignored because they were less likely to be adsorbed to grits compared to NP. Therefore, it is considered that the grit chamber had no influence on nonylphenolic compounds removal.

As can be seen from the mass balance of nonylphenolic compounds in WWTPs, output pathways of nonylphenolic compounds from WWTPs were summarized to be biodegradation, adsorption onto sludge and release via effluents. Comparing these results to other investigations, at least 60–65% of nonylphenolic compounds entering the Switzerland WWTPs (Ahel et al., 1994) were discharged into the environment via effluents and adsorption onto sludge, and 30–89% of the incoming nonylphenolic compounds in American WWTPs (Loyo-Rosales et al., 2007) were released by effluents and sludge, leaving 11–70% for microbial transformation. On the contrast, the four surveyed WWTPs of Beijing in this study released a smaller amount, 21.8–47.6% of the input nonylphenolic compounds into environment, indicating more nonylphenolic compounds were missing during biodegradation. Higher elimination efficiencies during biological treatment in these four WWTPs may be the result of low concentrations of nonylphenolic compounds in the influents, but needs further investigations.

For plant 1 and plant 4, the ratios of biodegradation amount to adsorption amount were 6.9 and 8.5, respectively, while for plant 2 and plant 3, the ratios were 1.3 and 3.0, respectively. It is important to note

Fig. 4. COD and total concentrations of NP-c in influents of plant 1 in dry and rain weather.

Fig. 5. Flow chart for a representative WWTP and nonylphenolic compounds mass balance in the four surveyed WWTPs. Q : flow rate of influent; Q_p : flow rate of primary sludge; Q_{ex} : flow rate of excess activated sludge; R : reflux ratio; Q' : supernatant stream of sludge area, amounting to $Q_p + Q_{ex}$.

that plant 2 and plant 3 possessed primary settling tanks. It is hypothesized that a great deal of nonylphenolic compounds were adsorbed onto sludge flocs in primary settling tanks before entering the biological treatment units, resulting in a larger amount via the adsorption pathway, thus leading to lower ratios of the amount biodegraded to that adsorbed. On the other hand, the total concentration of nonylphenolic compounds in primary sludge was 0.915 mmol/kg, exceeding the concentration in excess sludge (0.066 mmol/kg) greatly, which confirmed that primary sludge had significant adsorption to nonylphenolic compounds due to larger amount of input nonylphenolic compounds in the primary settling tank than that in the second settling tank. From the above it can be concluded that the primary settling tanks played an important role in the adsorption output pathway for nonylphenolic compounds during wastewater treatment process.

3.4. Output pathways of each group of NPnEOs metabolites in WWTPs

Except the sum of nonylphenolic compounds, the fates of each group of NPnEOs and their metabolites in the four WWTPs were shown in Fig. 6. As far as NP and NPnEOs ($n=1,2$) were concerned, biodegradation pathways accounted for $60 \pm 30\%$ and $59 \pm 26\%$ of the mass input, respectively, followed by the contribution accumulated in the excess sludge ($40 \pm 25\%$ and $41 \pm 27\%$, respectively), whereas a minor part ($1.8 \pm 1.2\%$ and $1.5 \pm 1.0\%$, respectively) was discharged via effluents. NP and NPnEOs ($n=1,2$) were inclined to congregate onto sludge flocs in contrast to other metabolites because of their higher hydrophobicities. It is noteworthy that in plants 2 and 3, the amounts of NP and NPnEOs ($n=1,2$) in the sludge were evidently larger than those in plants 1 and 4, probably due to the presence of the primary

Fig. 6. Mass balance of each group of nonylphenolic compounds in the four WWTPs.

settling tanks in plants 2 and 3 that allowed more compounds attached to sludge before being biodegraded. The amounts of these compounds in the sludge of the four WWTPs were shown in Table 4. Concentrations of three excess sludge samples were detected in each WWTP during one sampling event, and the listed data in Table 4 were the ranges of the results in the four WWTPs. Remarkable elevated concentrations of NP and NPnEOs ($n=1,2$) were identified in sludge after anaerobically stabilized, as a result of transformation products of NPnEOs ($n=3-15$) during sludge digestion. It was proved that NP and NPnEOs ($n=1,2$) were weakly estrogenic, with potencies between about 1×10^{-4} to 1×10^{-6} the activity of 17 β -oestradiol (Jobling and Sumpter, 1993). Therefore, Although contamination of nonylphenol in sewage sludge in China was less serious than other countries (La Guarkia et al., 2001; Pryor et al., 2002; Aparicio et al., 2007), it has provoked more and more attention because above 60% of the total sewage sludge was recycled to agricultural land (Soares et al., 2008).

Fig. 6 presents that NPnEOs ($n \geq 3$) were mainly biodegraded during the wastewater treatment process, being mineralized or transformed to their metabolites, while a considerable portion of NPnECs was emitted via effluents, resulting in the most part of the total nonylphenol compounds in effluents (Fig. 1b). It has been proposed that NPnECs, especially NPnECs ($n=1,2$) had the similar estrogenic activities to short-chain NPEOs (Jobling and Sumpter, 1993), so further work is needed in terms of evaluating the possible risks of effluents and developing related contamination control technologies in WWTPs.

4. Conclusions

The occurrence and fate of a comprehensive group of nonylphenol polyethoxylates and their metabolites were investigated in four Beijing WWTPs. Conclusions are made as follows:

Influent concentrations of the total nonylphenolic compounds ranged from 0.115 to 0.347 $\mu\text{mol/L}$, and the removals of these compounds in wastewater were as high as 75.7% to 90.8%, reflecting good elimination effects of existing wastewater treatment processes for nonylphenolic compounds. Higher temperature may accelerate

microbial transform of long-chain NPnEOs. The rain weather decreased nonylphenolic compounds input to WWTPs as well as COD by dilution, but had no remarkable impact on the removal efficiencies compared to those in the dry weather.

NPnEOs and their metabolites entering WWTPs were output mainly through three pathways: biodegradation, adsorption onto sludge and release via effluents. 21.8–47.6% of the input amount was emitted into environment via effluents and sludge, leaving a considerable portion of nonylphenolic compounds available for microbial transformation. The grit chamber had nothing to do with elimination of nonylphenolic compounds, while the primary setting tank played an important role on the adsorption pathway.

NP and NPnEOs ($n=1,2$) tended to adsorb onto sludge flocs because of their high hydrophobic properties, on the other hand, NPnECs occupied most of nonylphenolic compounds in effluents due to their relative hydrophilic properties, both of which could raise environmental risk. The future must lie in the elimination of the residual nonylphenolic compounds in wastewater and sludge, and advanced oxidation process could perhaps be added followed by biological wastewater treatment process, which needs further discussion.

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Table 4
Concentrations of NPnEOs ($n=0-2$) in sludge.

Sample source	Concentrations (mg/kg)		
	NP	NP1EO	NP2EO
Excess sludge	3.1–22.3	3.4–38.7	5.5–32.8
Sludge anaerobically stabilized	149.6–167.2	27.6–30.1	9.5–11.0

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