Occurrence and risk assessment of NP, BPA and TCS in sewage treatment plants

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Abstract. A long-term investigation, which covered 6 sampling campaigns over one year, was carried out to evaluate the occurrence, removal and risk of nonylphenol (NP), bisphenol A (BPA) and triclosan (TCS) in two full-scale sewage treatment plants (STPs) in Guangdong, South China. The target compounds were detected in every sample. The influent concentrations of NP were in the ppb level, while TCS in the ppt level. The seasonal variation in the influent was observed due to human consumption and the rainfall. Domestic sewage discharge was an important source of TCS to the STPs. Three kinds of endocrine disrupting compounds (EDCs) could not be completely removed in the STPs, and the activated sludge treatment process contributed to most of the removal of compounds. In addition, the oxic tank and the anaerobic tank both showed good removal performances for target EDCs. According to the results produced from the calculation of the risk quotient, in the STP1 effluents TCS could pose a high risk to the aquatic environment, and STP2 effluents existed high risk of estrogen activity.

1. Introduction
Endocrine disrupting compounds (EDCs) are identified as a class of exogenous endocrine disruptors in environment which can interfere with the endocrine system of humans and animals, leading to developmental and reproductive abnormalities [1,2]. EDCs comprise natural hormones, synthetic compounds and phytoestrogens secreted by humans and animals. Many investigations indicate that EDCs is ubiquitous in various environmental media, and its potential risks to biological and human beings are not underestimated [3-5]. In this context, EDCs has attracted worldwide attention because of its wide range of pollution and directly threaten.

Relative contributions of EDCs into the environment depend on efficacies of sewage treatment plants (STPs). The existing sewage treatment technique is designed for conventional pollutants, such as COD, BOD, nitrogen and phosphorus. EDCs which have complex molecular mechanism and unique biological chemistry can't be effectively removed by STPs [6,7]. The investigations were carried out to evaluate the occurrence of EDCs in STPs in many countries and regions of the world. A lot of work has been carried out with special respect to the actegories of strong endocrine active substances, such as ethylene female phenol, estrone, estradiol and ethinyl estradiol [8-11]. Few studies are available concerning the contribution of each treatment unit in EDCs removal by the STPs or conducted over long continuous periods of sampling time [12-14].
Nonylphenol, bisphenol A and triclosan have been shown to elicit endocrine disruptive effects [15]. The three kinds of EDCs are high production volume chemicals. The global demands expected to grow steady while the strongest growth will be in Asia, mainly China. Nonylphenol, bisphenol A and triclosan have been also detected in various environmental media in China [3,8,9,16]. The authors believed that more investigations are necessary to characterize these EDCs fate/transport in STPs, and ultimately, improve the environmental risk predictability.

To be a complement of previously published studies, the contamination levels of 3 EDCs including nonylphenol, bisphenol A and triclosan were investigated in two STPs of Guangdong, China. The first objective was to master the seasonal variation patterns of target EDCs in STPs. In addition, nonylphenol, bisphenol A and triclosan elimination contributions of each treatment unit were assessed. The survey data were also use to assess the possible environmental ecological risks.

2. Materials and methods

2.1. Chemicals

4-nonylphenol (NP), bisphenol-A (BPA), and triclosan (TCS) were used as chemical standards, whereas 4-n-nonylphenol (4-n-NP), [2H16] BPA (BPA-d16), and 13C-labeled triclosan (13C-TCS) were used as internal standards. Pentafluorobenzyl benzoyl chloride (PFBOCL, purity N99%) was used as derivatization reagent. HPLC-grade methanol, acetone, dichloromethane, n-hexane, toluene, triethylamine, pyridine and formic acid were used for sample processing and analysis. To avoid the contamination in the investigation, no plastics were used, and all glassware was baked for 4 h at 400°C before using.

2.2. Sampling campaigns

The basic operation parameters of the two STPs are shown in table 1.

| STP | Population Equivalent | Designed Treatment Capacity (m3/day) | Influent | HRT (h) | SRT (days) |
|-----|-----------------------|-------------------------------------|----------|---------|------------|
| ST P1 | 430000 | 72000 | municipal wastewater | 17 | 13 |
| ST P2 | - | 100000 | municipal wastewater, river water and industrial wastewater | 10 | - |

In STP1, four batches of wastewater samples were collected in campaign intervals of three months during the period from April 2011 to April 2012. Comparison with the feed wastewater for STP1 is the municipal wastewater, the feed wastewater for STP2 was replaced by municipal wastewater, river water and industrial wastewater in early 2012. In order to assess the effect of feed wastewater quality variation, sampling campaigns in STP2 were carried out in November 2011 and November 2012. Two grab samples were taken in each sampling campaigns in a.m. (10:00–11:30) and p.m. (16:00–17:30). The mean values of concentrations were used for the estimation of target EDCs. Filtered samples were stored at 4°C and extracted within 24 h.

2.3. Analytical methods

A previously developed multi-residue analytical method was used to measure the target EDCs in the study [16]. Agilent 6890N with 5975B GC-MS were used to analyze the concentrations of the target compounds.

3. Results and discussion
3.1. Occurrence in overall
The investigations involve six sampling periods, and 96 samples were collected. NP, BPA and TCS were found in every sample, with high detection frequencies (100%).

Table 2. Mean concentrations of NP, BPA and TCS in STP1 (ng/L).

| STP1                      | NP  | BPA | TCS |
|---------------------------|-----|-----|-----|
| Influent                  | 1554| 808 | 359 |
| Anaerobic plant           | 727 | 519 | 291 |
| Anoxic plant              | 644 | 475 | 298 |
| Oxic plant 1              | 564 | 241 | 349 |
| Oxic plant 2              | 443 | 312 | 323 |
| Horizontal settling tank  | 369 | 296 | 203 |
| Inclined-tube settling tank| 362| 302 | 222 |
| Effluent                  | 331 | 290 | 204 |

The mean concentrations of the three compounds in STP1 are shown in table 2. In influents, discrepant concentrations were observed. The most abundant compounds detected were NP (1554 ng/L) and BPA (808 ng/L) followed, while TCS (359 ng/L) was detected at the lowest concentrations. The concentrations of the same target compounds varied between the two STPs. The higher concentrations of NP and BPA were found in STP2 influents, whereas the higher concentrations of TCS in STP1. A similar conclusion that the concentration variation in influents was observed in different wastewater treatment plant have been reported [17,18]. In addition, it should be noticed that the inlet concentrations of NP were ris ed sharply in STP2, which coupled with the variation in feed wastewater quality (figure 1). NP was found in inlets at concentration of 25 μg/L in November 2011 and 86 μg/L in November 2012. Compared with the concentrations of BPA and TCS in inlets were decreased slightly. According to the further survey, the industrial wastewater of feed wastewater in STP2 mainly comes from the surrounding dyeing houses and rinse factories. These factories are using nonylphenol polyoxyethylene ether (NPEOs) as the main raw material and result in the production wastewater containing high concentrations of NP. We can be speculated that the environmental concentrations of NP will be at high value level.

NP, BPA and TCS were identified cannot completely removed by sewage treatment plants. Unlike the concentration profiles of target EDCs were variation in the influents, no significant differences were observed in the effluents. In STP1, NP, BPA and TCS were found in outlets at individual mean concentrations of 331 ng/L, 290 ng/L and 204 ng/L, respectively.
3.2. Occurrence in seasonal variation in STP1
Seasonal variation in the concentrations of NP, BPA and TCS in the STP1 was shown in figure 2. In the influents, NP, BPA and TCS were observed discrepant seasonal variations, which can be mainly associated with the human usage and the wet and dry seasons. The behavior carried out in various treatment process section and the effluents was restricted to feed concentrations, but mainly affected by the removal effect of the sewage treatment process.
NP and BPA showed the highest concentrations in January in the STP1 influents. NP as a kind of surfactant is widely used in industrial washing products. BPA is used in polymer materials industrial products such as polycarbonates (PC) and epoxy resin. Therefore, relative contributions of NP and BPA to surface waters mainly depend on human production activities. In order to complete the annual production targets, factories tend to increase production at the end of the year, and result in the amount of pollutants such as NP and BPA increases significantly. The concentrations of TCS in the STPs influents were mainly determined by the use of personal care products in daily life, so there would be no seasonal peak. The lowest level of concentrations of TCS was observed in July, due to the typhoon season. However, there was no similar phenomenon in NP and BPA, and the concentration nadir of BPA in April could not be explained.

As shown in figure 2, no obvious seasonal variation was presented in each treatment unit, and also in the effluents. BPA showed the highest concentrations in January in the STP1 influents and in July in the effluents. Comparison with the overall removal efficiencies of BPA in the STP1 were 81.8% in January and 31.4% in July, respectively (table 3). These results clearly reflected the removal effect is the main factors influencing the effluents. The efficiency of STPs is related to various factors, such as the initial concentrations of the target compounds, the physical and chemical properties of the target compounds, the molecular structure, treatment technology used, operation parameters, etc. The concentrations of these compounds were reported to be larger in winter than in summer, and the efficiency of STPs was found to be slightly higher in summer due to the high environment temperature [19]. Guangdong is located in southern coast of China, has a subtropical climate with the mean annual temperature above 20°C. Depends on the small annual temperature difference, there were no significant seasonal variation observed in the effluents.

| Table 3. Remove efficiencies of NP, BPA and TCS in STP1 and STP2. |
|---------------------------------------------------------------|
| Removal efficiency (%) | **STP1** | **STP2** |
| | 2011/04 | 2011/07 | 2011/10 | 2012/01 | 2011/11 | 2012/11 |
| NP | 83.6 | 70.8 | 77.1 | 80.7 | 98.6 | 80.2 |
| BPA | 89.2 | 31.4 | 54.8 | 81.8 | 99.7 | 99.4 |
| TCS | 35.7 | 45.4 | 42.6 | 48.8 | 76.0 | 80.9 |

3.3. Removal efficiency of EDCs
The removal efficiencies for NP, BPA and TCS in the STP1 and STP2 are given in table 3, and their average removal efficiencies are given in figure 3. Compared with STP1, the removal rates of the three compounds were presented more stable in STP2. The average total removal rates of the target EDCs in STP1 was in a sequence of NP (78.7%) > BPA (64.1%) > TCS (43.0%).

Figure 3. The removal efficiencies for selected compounds in STP1 and STP2.
The sewage treatment plants usually consist in primary treatment and secondary treatment (activated sludge treatment), and some STPs will set up the depth treatment before the discharge. To further study the performance of various treatment process, the concentrations of NP, BPA and TCS in different treatment tanks of STP1 and STP2 were analyzed to determine their removal contributions (see figure 3). Except the analysis data of NP in STP2 is single sampling data (2011-11), the mean values of the repeatedly sampling data were used for the estimation of target EDCs.

As shown in the figure 3, activated sludge played an important role in the removal of the target EDCs. In this study, the anaerobic tank revealed to be the most important tanks for EDCs elimination, the aerobic tank followed, whereas the anoxic tank and the sedimentation tank most likely made a negligible contribution. In the anaerobic tank, the reduction of NP, BPA and TCS is mainly attributed to the sludge-adsorption [20]. And the anaerobic biodegradation was also considered to be an important factor. In order to effectively dispel nitrogen, part of the biochemical treatment effluents would be transferred back into anaerobic period. This technology strategy might dilute the target compounds concentrations. The mechanism of the activated sludge precipitation could be involved to explain the reduction of the investigated EDCs after the setting tank. While the presence of EDCs conjugates could be involved to explain the increase after the setting tank and the anoxic tank [21,22].

3.4. Risk assessment
In order to estimate the Environmental risk of the target EDCs in effluent wastewater, the risk quotient (RQ) approach was chosen. This quotient is calculated as the ratio between Measured Environmental Concentrations (MEC) and Predicted No-Effect Concentrations (PNEC).

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RQ = \frac{\text{MEC}}{\text{PNEC}} = \frac{\sum C_{\text{out}} \times \text{EEQ}}{\text{PNEC}}
\]

Where, MEC is expressed as measured environmental concentrations. PNEC is expressed as predicted no-effect concentrations. \(C_{\text{out}}\) is the maximum concentrations of the target compound in the effluents. EEQ is expressed as estradiol equivalent. Since the EEQ value for TCS is extremely low, MEC value correspond to maximum levels detected for TCS in order to assess Environmental risk. In this context, the PNEC values for the target pharmaceuticals were adopted from Zhao et al [23].

|          | PNEC (ng/L) | MEC(ng/L) | RQ |
|----------|-------------|-----------|----|
|          | STP1        | STP2      | STP1 | STP2  |
| NP       | 1.5         | 0.076     | 1.713 | 0.05  | 1.14  |
| BPA      |             |           |       |       |       |
| TCS      | 50          | 245       | 21    | 4.90  | 0.42  |

As shown in table 4, the environmental risk assessment of estrogen activity for NP and BPA indicated minimal risk (RQ<0.1) in STP1 effluents, and indicated high risk (RQ≥1) in STP2 effluents. TCS could pose a high risk (RQ≥1) to the aquatic organisms in STP1 and a medium risk (0.1≤RQ<1) in STP2. This evaluation, however, is only focused on the three EDCs, but in the aquatic environment, there are a wide variety of EDCs which are present as stronger complex toxicity.

4. Conclusions
In this work, three EDCs were investigated in two sewage treatment plants. In the influents, the most abundant EDCs detected was NP, BPA followed, and TCS was detected at the lowest concentrations. Seasonal variations for NP and BPA in influents were observed. The lowest concentrations of TCS were found in the summer due to consumption and rainfall. Compared with STP1, the removal rates of
the three compounds were presented more stable in STP2. The anaerobic tank showed good removal performances for target EDCs, the aerobic tank followed, but the anoxic tank and the sedimentation tank most likely made a negligible contribution. Finally, according to environmental risk assessment data, there was an environmental risk of estrogenic activity for NP and BPA in STP2 and a high risk for TCS in STP1.

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References
[1] Harshbarger J C, et al 2000 Intersexes in Mississippi River shovelnose sturgeon sampled below Saint Louis, Missouri, USA Mar. Environ. Res. 50 247-50
[2] Blazer V S, et al 2007 Intersex (testicular oocytes) in smallmouth bass from the Potomac River and selected nearby drainages J. Aquat. Anim. Health 19 242-53
[3] Li Y, et al 2012 Spatial distribution of three endocrine disrupting chemicals in sediments of the Suzhou Creek and their environmental risks Chinese J. Environ. Sci. 33 239-46 (In Chinese)
[4] Zhang S, et al 2007 Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA Chem. 66 1057-69
[5] Fairbairn D J, et al 2016 Sources and transport of contaminants of emerging concern: A two-year study of occurrence and spatiotemporal variation in a mixed land use watershed Sci. Total Environ. 551–552 605-13
[6] Ying G G, et al 2002 Environmental fate of alkylphenols and alkylphenol ethoxylates - a review Environ. Int. 28 215-26
[7] Melvin S D and Leusch F D L 2016 Removal of trace organic contaminants from domestic wastewater: A meta-analysis comparison of sewage treatment technologies Environ. Int. 92-93 183-8
[8] Hu J Y, et al 2007 Fate of endocrine disrupting compounds in membrane bioreactor systems Environ. Sci. Technol. 41 4097-102
[9] Xu N, et al 2012 Removal of estrogens in municipal wastewater treatment plants: A Chinese perspective Environ. Pollut. 165 215-24
[10] Pessoa G P, et al 2014 Occurrence and removal of estrogens in Brazilian wastewater treatment plants Sci. Total Environ. 490 288-95
[11] Belhaj D, et al 2015 Fate of selected estrogenic hormones in an urban sewage treatment plant in Tunisia (North Africa) Sci. Total Environ. 505 154-60
[12] Archer E, et al 2017 The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit drugs in a WWTW and environmental waters Chem. 174 437-46
[13] Nakada N, et al 2007 Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant Water Res. 41 4373-82
[14] Komesli O T, et al 2015 Occurrence, fate and removal of endocrine disrupting compounds (EDCs) in Turkish wastewater treatment plants Chem. Eng. J. 277 202-8
[15] Kolpin D W, et al 2002 Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance Environ. Sci. Technol. 36 1202-11
[16] Zhao J L, et al 2009 Determination of phenolic endocrine disrupting chemicals and acidic pharmaceuticals in surface water of the Pearl Rivers in South China by gas chromatography negative chemical ionization–mass spectrometry Sci. Total Environ. 407 962-74
[17] Vogelsang C, et al 2006 Occurrence and removal of selected organic micropollutants at
mechanical, chemical and advanced wastewater treatment plants in Norway Water Res. 40 3559-70

[18] Cespedes R, et al 2008 Occurrence and fate of alkylphenols and alkylphenol ethoxylates in sewage treatment plants and impact on receiving waters along the Ter River (Catalonia, NE Spain) Environ. Pollut. 153 384-92

[19] Sui Q, et al 2011 Seasonal variation in the occurrence and removal of pharmaceuticals and personal care products in different biological wastewater treatment processes Environ. Sci. Technol. 45 3341-8

[20] Tang Y, et al 2014 Removal of naproxen and bezafibrate by activated sludge under aerobic conditions: Kinetics and effect of substrates Biotechnol. Appl Bioc. 61 333-41

[21] Vieno N, et al 2007 Elimination of pharmaceuticals in sewage treatment plants in Finland Water Res. 41 1001-12

[22] Radjenovic J, et al 2007 Advanced mass spectrometric methods applied to the study of fate and removal of pharmaceuticals in wastewater treatment Trac-trend. Anal. Chem. 26 1132-44

[23] Zhao J L, et al 2010 Occurrence and a screening-level risk assessment of human pharmaceuticals in the Pearl River system, South China International Symposium on Environmental Toxicology and Environmental Chemistry - Asia Pacific Section C pp 1377-84