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Occurrence and assessment of treatment efficiency of nonylphenol, octylphenol and bisphenol-A in drinking water in Taiwan

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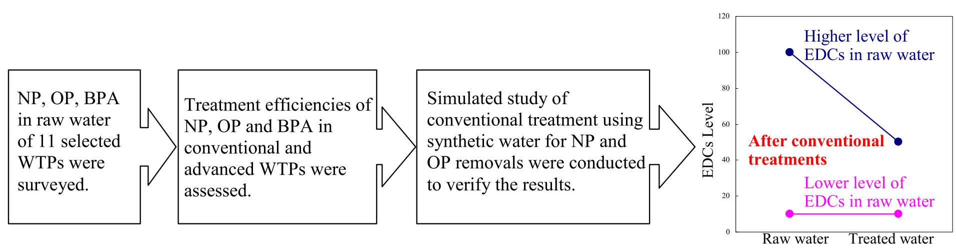
HIGHLIGHTS

- ► NP, OP, and BPA were identified in most of the sampled water sources.
- ► Efficiencies of NP, OP, and BPA in conventional treatment processes evaluated.
- ► Higher NP treatment efficiency was obtained when NP in raw water were high.
- ► Chlorination plays an important role in NP degradation in water.

GRAPHICAL ABSTRACT



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ABSTRACT

Occurrence and methods for the removal of nonylphenolic compounds in drinking water have been gaining increased attention due to their widespread presence in natural water and the potential health risks from the consumptions of drinking water. The purpose of this study was to assess the occurrence of nonylphenol (NP), octylphenol (OP), and bisphenol-A (BPA) in water sources and treated water in Taiwan, to evaluate the treatment efficiencies of these compounds in both the conventional (coagulation, sedimentation, filtration and chlorination) and advanced treatment processes. The treatment efficiencies of these chemicals were assessed based on their concentrations in water sources, and the results were verified with laboratory simulated treatment processes. A survey of NP, OP, and BPA in 11 Taiwanese water sources showed that all of them could be identified in most of the sampled sources, and that higher concentrations of NP were found when the raw water was contaminated by domestic wastewater. However, higher treatment efficiency could be observed when the NP concentration in water source is high. Laboratory simulation studies of conventional treatment processes showed that chlorination played an important role in the degradation of NP in raw water. Treatment efficiencies of 60%–90% were achieved for NP removal when sufficient chlorine dosages were applied to satisfy chlorine demands. However, results also showed that conventional coagulation and rapid filtration processes were less effective in the reduction of phenolic compounds in water.

1. Introduction

The presence of endocrine disrupting compounds (EDCs) in drinking water has in recent years drawn public attention to their potential estrogenic effects in humans. The most frequently detected chemicals among the various EDCs include bisphenol-A (BPA) and

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some nonylphenolic compounds such as 4-nonylphenol (NP) and 4-tert-octylphenol (OP). The harmful effects of nonylphenol on estrogenic characteristics were first discovered during laboratory experiments on natural estrogens in animals (Soto et al., 1991). NP and OP exhibits about 10^{-5} and 3×10^{-5} the estrogenic activity of 17β-estradiol, and BPA has 10^{-4} potency of estradiol (Witorsch, 2002; Jobling and Sumpter, 1993). Advances in analytical methods have increased detection of trace chemicals in various environmental matrices including drinking water. Based on the results of numerous studies concerning their wide spread, both NP and OP have been included in the priority list of hazardous substances in water by the European Union (EU Environmental Quality Standards Directive(EQSC), 2008). Due to the wide spread and potential threat of these chemicals to human health, both NP and BPA have been included in the Drinking Water Contaminant Candidate List by the Taiwan Environmental Protection Administration.

Nonylphenol ethoxylates (NPEOs) and octylphoenol ethoxylates (OPEOs) are two of the most prevalent groups of nonionic surfactants in the environment (Ferguson et al., 2001). Due to their octanol/water partition coefficient, NPEOs and OPEOs can be expected to be adsorbed by particles in wastewater effluents, river water, and sediments. In biodegradation pathways NPEOs and OPEOs were broken down to alkylphenol acetic acids by ω-carboxylation of EO chains and underwent subsequent aerobic degradation and transform to NP and OP (Jonkers et al., 2001). Besides being a metabolite of NPEOs, NP is also a manufactured reagent. Both NP and OP can enter the environment through human activities, especially via treated wastewater effluents and direct discharge from e.g. pesticide applications (Ying et al., 2002). Human exposure to NP and OP can also occur via drinking water and food consumptions (Shao et al., 2005). A tolerable daily intake (TDI) value of NP was set at 0.005 mg/kg body weight (Nielsen et al., 2000); however, no TDI of OP is available.

A proportion of NP was adsorbed to particles in water due to its high K_{oc} value. A Japanese study found that about 80% of NP and 60% of OP in primary treated effluent was in the particulate phase, while percentages were around 30% and 10%, respectively, in biologically treated effluent, and 20% and 10% in river water (Isobe et al., 2001). Studies conducted in Japan, Spain, Canada, USA, and Germany found concentrations of NP in river water ranging from undetectable to 17.5 μg/L (Bennie et al., 1997; Cespedes et al., 2008; Isobe et al., 2001; Kolpin et al., 2002). OP concentration was about 10 times lower than that of NP and undetectable in some samples. The NP concentration was ranging from 0.1 to 1 μg/L in drinking water (Li et al., 2010; Loos et al., 2007). In Taiwan, concentrations of NP as high as 657 ng/L were found in the treated effluent of domestic wastewater treatment plants, and values of up to 4022 ng/L were found in highly polluted river water (Lien et al., 2009). In another study, NP was found at μg/L levels in five major rivers from northern to southern Taiwan (Cheng et al., 2006; Ding and Wu, 2000). The Taiwan EPA has banned the usage of NP in domestic detergent production since 2009 for aquatic environmental protection reasons.

BPA is an important raw material in the production of polyacrylates, polyesters, epoxy resins, and polycarbonate plastics (Basheer et al., 2004). Since these compounds have the properties of high impact strength, transparency, resistance to acids, stability in oil and temperatures between −40 °C and 145 °C, they have been widely used in automobile parts manufacturing, adhesives, protective coatings, PVC pipe coatings, food packaging, and plastic bottles. Their increasing use has led to the presence of BPA in aquatic environments such as wastewater, rivers, and even water sources. BPA is relatively difficult to be degraded under aerobic conditions, as compared to NP and OP (Ying et al., 2003). Current treatment plant operation units cannot completely remove BPA from industrial wastewater. Treatment efficiency for BPA ranged from 37% to 94%, suggesting that industrial effluents from industries were the main source of BPA contamination in the aquatic environment. According to studies conducted in the USA, Germany, Japan, and the Netherlands, BPA concentrations were mostly ranging from not detectable to 1 μg/L in river water (Flint et al., 2012). In drinking water in Italy and Malaysia, BPA levels were reportedly between 17 to 56 ng/L and 3.5 to 59.8 ng/L, respectively (Kang et al., 2006; Santhi et al., 2012). The European Food Safety Authority has set a TDI of BPA at 0.05 mg/kg body weight (EFSA, 2006).

Most of the studies focused on the variations of the NP and BPA concentrations between drinking water and raw water; however, the treatment efficiency through the conventional treatments in WTP was seldom discussed. The main objectives of this study were: 1) to investigate the concentration distributions of NP, OP, and BPA in water sources and treated water in Taiwan; 2) to evaluate the treatment efficiencies of these EDC compounds in both conventional and advanced water treatment plants; 3) to assess treatment efficiencies of these chemicals based on their concentrations in water sources; and 4) to investigate the effectiveness of elimination of these compounds with simulated water treatment processes.

2. Materials and methods

2.1. Chemicals and reagents

Nonylphenol technical mixture, 4-octylphenol (4-OP), 4-*tert*-octylphenol (OP), bisphenol-A, and formic acid were purchased from Sigma-Aldrich (purity > 98%). Bisphenol A-d_{16} (internal standard) was obtained from Supelco (purity > 98%). HPLC-grade methanol, dichloromethane, acetone, and n-heptane were purchased from Riedel-de Haën. N-methylmorpholine was provided by Aldrich (purity > 99.5%). Sodium hypochlorite was purchased from Riedel-de Haën. Sodium thiosulfate pentahydrate and aluminum sulfate ($Al_2(SO_4)_3\cdot13\text{-}14H_2O$) were purchased from Wako and Nacalai Tesque, respectively. All standards were prepared in methanol and stored at 4 °C before use.

2.2. Sample collection

Water samples were collected from 11 water treatment plants (WTPs), including conventional treatment plants (C-WTPs) and WTPs with advanced treatment units (A-WTPs) in different regions of Taiwan. Conventional treatment processes in Taiwan's WTPs include pre-chlorination, coagulation, sedimentation, filtration, and post-chlorination. Advanced treatment units as ozonation, membrane filtration, and active carbon absorption are applied in some A-WTPs according to their raw water quality. To facilitate the comparison of treatment efficiency in WTPs, sampling locations in each WTP included raw water, sedimentation unit, filtration unit, and a point after post-chlorination. In most WTPs, pre-chlorination and coagulation/flocculation are carried out at the same unit, followed by the sedimentation unit. Therefore, samples taken after sedimentation are used to represent pre-chlorination, coagulation, and sedimentation. Raw water qualities of the selected WTPs are shown in Table 1. A total of 282 samples were collected from April 2009 to October 2011. These sampling points were chosen to evaluate the treatment efficiencies after each treatment unit. Water samples were collected with pre-cleaned 1 L amber glasses and pH was adjusted to <2.5 with formic acid for preservation. In water samples, pH was between 6.5 and 8.9 and temperatures between 18 and 35 °C when sampled. All samples were stored at 4 °C and were extracted within 14 days of sampling.

2.3. Simulated water treatment processes

Water treatment processes were simulated in the laboratory. Conventional treatment processes adopted by most water utilities in Taiwan, include pre-chlorination, coagulation, sedimentation, rapid filtration, and post-chlorination of laboratory synthetic raw water. Milli-Q water and 5 μm filtered eco-pond water from National