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Research Paper

Biocides in wastewater treatment plants: Mass balance analysis and pollution load estimation

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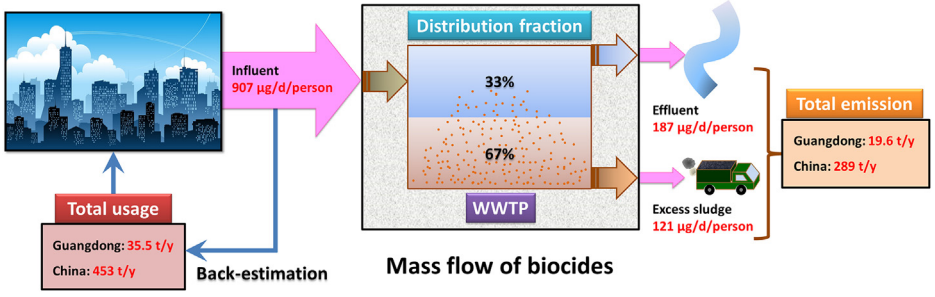
HIGHLIGHTS

- Biocides were detected widely in the WWTPs and their receiving rivers.
- Most biocides were readily removed from the liquid phase of WWTPs.
- Biocide removal attributed to the degradation and adsorption onto sludge.
- The back-estimated usage of ∑19 Biocides was up to 453 t/y in the whole China.
- The emission of ∑19 Biocides was 308 μg/d/person for effluent plus excess sludge.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aimed to investigate the occurrence and removal of 19 biocides in ten different wastewater treatment plants (WWTPs), then estimate the usages and emissions per capita of 19 biocides based on mass balance analysis approach. The results showed that target biocides were universally detected in the WWTPs and their receiving rivers, and 19 for liquid samples and 18 for solid samples. The prominent compound for liquid was DEET (*N,N*-diethyl-3-methylbenzamide), with its maximum concentration of 393 ng/L in influent; while that for solid was triclocarban with its maximum concentration of 2.11×10^3 ng/g in anaerobic sludge. Most biocides were readily removed from the liquid phase of ten WWTPs, and the mean removal rate to ∑19 biocides was up to 75%. The removals of target biocides were attributed to biodegradation and adsorption onto activated sludge. The mean input per capita for ∑19 biocides based on influent was 907 μg/d/person, while the emissions per capita were 187 μg/d/person for effluent, and 121 μg/d/person for excess sludge. As demonstrated, the biocides contamination of the receiving rivers could pose potential ecological risks for aquatic organisms. Therefore, advanced wastewater treatment technologies should be developed to reduce the emission of biocides into the receiving environment.

1. Introduction

Biocides are defined as a class of active substances used for destroying or inhibiting any harmful organisms, but are harmless to human beings [1]. According to their usage pattern, they are classed

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into five categories: disinfectants, preservatives, pest control (e.g. insect repellents), and other biocidal products (e.g. antifouling agents) [1,2]. These chemicals are widely used at high dosage in various pharmaceuticals and personal care products (PPCPs) [3,4]. For example, parabens were used at various rinse-off products and leave-on products, with their highest concentrations on the order of mg/g of the products including [5]. The azole fungicide climbazole is usually used in anti-dandruff shampoos, with the maximum content of 2.0% [6], while other fungicides (e.g., clotrimazole, ketoconazole and miconazole) are usually administered as ointment or oral anti-fungal medications, with the content range of 1–2% in formulations [7]. In recent years, biocides have been frequently detected in the surface water and sediment [8,9] and the biosolid-amended soils [10,11], and the maximum concentration were up to the order of magnitude of μg/L [12,13] and μg/g, dry weight (dw) [14,15], respectively. The high concentration levels of biocides present in the receiving environment can cause some adverse effects to many organisms, and even human beings [16], such as general toxicity [17,18], bioaccumulation [19,20] and endocrine disrupting effects [21,22]. Therefore, it is essential to understand the removal of various biocides in wastewater treatment plants (WWTPs) and their emissions into the receiving environment.

According to some previous studies, municipal wastewater is regarded as the main emission source for biocides into the receiving environment [9,23,24]. After use of the products containing biocides, a mass of biocides were discharged into wastewater and then reached WWTPs through sewer network [25–27]. Therefore, various biocides were frequently detected in the influent and effluent of WWTPs [9,25,28], and their concentration levels in the sewage (sludge) of WWTPs varied among different process types and different regions, usually falling in the range from several tens to thousands ng/L (ng/g) [2,29–31]. Generally, biocides cannot be removed completely by conventional treatment technologies, with removal rates ranging from 0% to almost 100% [9,26,30,32]. These previous reports mainly focus on a few or a class of biocides, or are limited in the investigation of only influent or effluent of a few WWTPs with same or similar treatment technologies. Currently, there is lack of a systematic investigation into the occurrence, removal, mass balance and pollution loads of different classes of biocides in WWTPs with different treatment technologies.

The aim of this study was to investigate the occurrence and removal of 19 target biocides in ten WWTPs of Guangdong province, South China. Further, mass balance analysis was applied to estimate their mass loads in the different process stages and to reveal their removal mechanisms. The usages and emissions of these biocides in the region were calculated based on their pollution loads in ten WWTPs. The results from this study can facilitate better understanding of the fate of various biocides in different WWTPs, and assess their elimination efficiencies in seven different wastewater treatment technologies. Moreover, the estimated pollution loads of biocides can provide much needed data to assess their potential ecological risks.

2. Materials and methods

2.1. Chemicals

The target compounds selected in this study were 19 common biocides, including: 8 fungicides, 2 insect repellents, 3 isothiazolinone antifouling agents, 4 preservatives and 2 disinfectants. The basic physico-chemical properties of these biocides are listed in Table S1 (Supplementary material), and their chemical structures are shown in Fig. S1. Eleven internal standards for the 19 target biocides were obtained from various suppliers. The supplier sources of all the chemicals and reagents are given in Text S1. Individual stock solutions of all target compounds and internal standards were prepared with methanol in amber glass bottles and kept at −18 °C.

2.2. Sampling site and sample collection

Ten WWTPs selected in this study are located in Guangzhou, Dongguan and Huizhou of Guangdong province, South China. The basic information of ten WWTPs is listed in Table 1. The treatment technologies applied in the WWTPs include A^2/O (Anaerobic-Anoxic-Oxic), reversed A^2/O, modified A^2/O, modified A/O (Anaerobic-Oxic), MBR (Membrane Bio-Reactor), Carrousel 2000 Oxidation ditch and UNITANK (Combination alternating activated sludge process). The technical flow chart and the sampling points for each WWTP are shown in Fig. S2. Wastewater in each process stage, activated sludge in biochemical stages, return sludge and excess sludge were collected. It should be noted that the WWTPs received separated sewer system water. Meanwhile, the surface water and sediment in the receiving rivers were also collected from the upstream/downstream sites of 100 m far from the outlet of WWTPs.

Sampling campaigns were carried out during the period of May to October in 2015. All the samples for each WWTP were collected as 24 h flow integrated composite samples, while the surface water and sediment samples were grabbed once in the middle of the sampling day, and three replicates were obtained for each type of sample at each site. For each replication, the total volume of each sample was 1L for water sample, approximately 1L for the activated sludge and return sludge after filtering, and 0.5 L for the excess sludge and sediment. After sampling, the pH value of water sample was adjusted to 3.0 by 4 M H_2SO_4, then added with 5% methanol (v/v) to inhibit microbial growth. Sodium azide (1 g/L each) was added into sludge/sediment sample to suppress potential microbial activity. Then, all the samples were placed in cool-boxes, transported to laboratory and stored in a 4 °C cold room before processing. The water samples were processed within 48 h. The sediment samples were homogenized and passed through a 0.83 mm mesh after lyophilizing, then placed in glass bottles, and finally stored at 4 °C until the extraction.

In addition, basic quality parameters were measured for the influent, effluent and excess sludge samples of each WWTP and the surface water and sediment samples from receiving rivers. For the water samples, the BOD_5 (biochemical oxygen demand for 5 days), COD (chemical oxygen demand), TP (total phosphorus), TN (total nitrogen) and NH_3-N (ammonia-nitrogen) were measured according to the reported methods [33]; their pH, conductivity and DO (dissolved oxygen) were monitored on site by a YSI-Pro2030 multi-parameter water quality monitor (YSI Incorporated, USA). For sludge and sediment samples, TP, TN and NH_3-N were determined similarly as water samples after digestion (TP and TN) and KCl solution extraction (NH_3-N), and the TOC (total organic carbon) was analyzed by a LiquiTOC analyzer (Elementar Analysensyteme Co., Germany). The results of water quality parameters and the removal rates of conventional pollution indicators are given in Table S2, and the sediment quality parameters in Table S3.

2.3. Sample extraction and instrumental analysis

Nineteen target biocides in wastewater, surface water, sludge and sediment samples were extracted and analyzed according to our previous method [2]. Briefly, water samples (1 L each) were filtered through 0.7 μm glass fiber filters, and spiked with 100 ng of an internal standard mixture (100 μL, 1 mg/L each). Then, the samples were extracted by the solid phase extraction method using HLB cartridges (500 mg, 6 mL), which were preconditioned consecutively with 10 mL methanol and 10 mL Milli-Q water before use. The target compounds were eluted from each cartridge with ethyl acetate