ARTICLE IN PRESS
MPB-07970; No of Pages 5
Marine Pollution Bulletin xxx (2016) xxx–xxx
Contents lists available at ScienceDirect
Marine Pollution Bulletin
journal homepage: www.elsevier.com/locate/marpolbul

A novel approach for estimating the removal efficiencies of endocrine disrupting chemicals and heavy metals in wastewater treatment processes

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ARTICLE INFO

Article history:
Received 30 April 2016
Received in revised form 10 August 2016
Accepted 18 August 2016
Available online xxxx

Keywords:
Artificial Mussel
Endocrine disrupting chemical
Heavy metal
Removal efficiency
Semi-permeable membrane device

ABSTRACT

The wide occurrence of endocrine disrupting chemicals (EDCs) and heavy metals in coastal waters has drawn global concern, and thus their removal efficiencies in sewage treatment processes should be estimated. However, low concentrations coupled with high temporal fluctuations of these pollutants present a monitoring challenge. Using semi-permeable membrane devices (SPMDs) and Artificial Mussels (AMs), this study investigates a novel approach to evaluating the removal efficiency of five EDCs and six heavy metals in primary treatment, secondary treatment and chemically enhanced primary treatment (CEPT) processes. In general, the small difference between maximum and minimum values of individual EDCs and heavy metals measured from influents/effluents of the same sewage treatment plant suggests that passive sampling devices can smooth and integrate temporal fluctuations, and therefore have the potential to serve as cost-effective monitoring devices for the estimation of the removal efficiencies of EDCs and heavy metals in sewage treatment works.

1. Introduction

1.1. Risks posed by endocrine disrupting chemicals and heavy metals in sewage

In the past few decades, many new chemicals have been developed and used extensively in a wide spectrum of domestic and industrial applications. Some of these, known as endocrine disrupting chemicals (EDCs), can affect endocrine systems and result in reproductive and developmental impairments in living organisms, including humans, even at very low concentrations (Bergman et al., 2012). For example, 4-nonylphenol (4-NP), a widely used surfactant in industrial and agricultural industries, exhibits strong estrogenic activities (Vetillard and Bailhache, 2006); Bisphenol A (BPA), a surfactant commonly used in the manufacture of plastics and epoxy resins, is both estrogenic and anti-androgenic (Calafat et al., 2008); Triclosan (TCS), an antibacterial agent used in a variety of personal care products, has been shown to disrupt human endocrine systems through activation of the pregnane X receptor (Raut and Angus, 2010); 17β-estradiol (E2), a natural estrogen produced by humans, as well as 17α-ethinylestradiol (EE2), a synthetic estrogen used in contraceptives, are transported in relatively large quantities into wastewater through urine (Balest et al., 2008) and may impair fish reproduction (Nash et al., 2004). The aforementioned EDCs have been shown to be widespread and persistent in aquatic environments, posing a significant threat to environmental and public health (Bergman et al., 2012, 2013).

Apart from EDCs, heavy metals including cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) are often present in significant concentrations in industrial wastewater due to mining, smelting, tanneries, electroplating, battery manufacture, petroleum refining, paint manufacture, inclusion in pesticides, pigment manufacture, and the printing and photographic industries (Kadirvelu et al., 2001). Extensive studies have shown that heavy metals can pose a threat to aquatic organisms and human health in view of their toxicity, bioavailability and non-biodegradability (Barakat, 2011). EDCs and heavy metals are commonly found in municipal and industrial

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http://dx.doi.org/10.1016/j.marpolbul.2016.08.043
0025-326X/

Please cite this article as: Chiu, J.M.Y., et al., A novel approach for estimating the removal efficiencies of endocrine disrupting chemicals and heavy metals in wastewater treatmen..., Marine Pollution Bulletin (2016), http://dx.doi.org/10.1016/j.marpolbul.2016.08.043

wastewaters, and have formed a major source of contamination in aquatic environments (Guo et al., 2009; Liang et al., 2011; Manickum and John, 2014; McAdam et al., 2010; Nies, 1999; Yang et al., 2012).

1.2. Problems with traditional approaches in estimating removal efficiencies

Currently, the removal efficiencies of EDCs and heavy metals in sewage treatment processes are determined and monitored by collecting and analyzing influent and effluent samples on a regular basis. Two problems arise from this approach. Firstly, the typically very low concentrations of pollutants (especially EDCs) present a major challenge in their sampling and chemical analysis. Secondly, it is not cost-effective or practical to perform frequent sampling and analysis, given the considerable fluctuation in concentrations of pollutants in the influent and effluent over relatively short periods. Biomonitors (e.g. mussels and oysters) have often been used to monitor pollutants in water since they can accumulate pollutants over time and provide a time-integrated estimate of pollutant concentrations in the aquatic environment (Phillips and Rainbow, 1993). However, this approach cannot be applied to sewage effluents since the concentrations of pollutants in biomonitors can be affected by a variety of physical and biological factors and, more importantly, biomonitors usually cannot survive in highly polluted environments such as sewage outfalls (Degger et al., 2011; Richardson et al., 2001; Wu et al., 2007).

Previous studies have shown that semi-permeable membrane devices (SPMDs) can provide a reliable time-integrated estimate of the concentrations of lipophilic compounds in aquatic environments, especially for organic compounds with K_{ow} values between 3 and 6 (Stuer-Lauridsen, 2005). In addition, the variability of accumulation in SPMDs is often much lower than that of biomonitors (Richardson et al., 2003). Similarly, both laboratory and field studies have demonstrated that Artificial Mussels (AMs) can provide a reliable time-integrated estimate of soluble metal concentrations in different hydrographic environments, including highly polluted areas (Gonzalez-Rey et al., 2011; Leung et al., 2008; Wu et al., 2007). Capitalizing on the advantages conferred by these passive monitoring devices, the present study aimed to use SPMDs and AMs to provide an initial evaluation of the removal efficiency of EDCs and heavy metals in three different sewage treatment processes (i.e. primary treatment, chemically enhanced primary treatment and secondary treatment). The study also validated the use of SPMDs and AMs as a practical and cost-effective method for determining and monitoring the removal efficiencies of EDCs and heavy metals in sewage treatment processes.

2. Materials and methods

2.1. Experimental design

Three sewage treatment plants (STPs) with different treatment processes (viz. primary treatment, chemically enhanced primary treatment and secondary treatment) in Hong Kong were selected for determining the removal efficiencies of EDCs and heavy metals. The characteristics of these STPs are provided in Table 1. In each STP, one SPMD unit and one basket of AMs were deployed at the influent channel, and another identical set of SPMDs and AMs were deployed at the effluent channel (both 1 m below water surface) in March 2012 for about a month. Each SPMD unit consisted of four individually sealed polyethylene SPMD tubes (1 m long, infused with 0.65 g purified triolein) housed inside a stainless steel canister (diameter: 14 cm; height: 20 cm). Each basket of AMs consisted of 15 AMs secured within a plastic basket (28 cm × 21 cm × 15 cm). Following retrieval, SPMD tubes were wrapped in pre-cleaned aluminum foil and AMs were sealed with damp cotton pads and put into plastic zipper bags, which were stored in an ice box and transported to the laboratory for chemical analysis.

2.2. Analysis of endocrine disrupting chemicals

Concentrations of 4-NP, TCS, BPA, E2, EE2 in each of the SPMD tubes were analyzed, following the methods described by Richardson et al. (2003) with minor modifications. Briefly, the surface of SPMDs was gently cleaned with Milli-Q water before being cut opened, and the triolein collected by drip-washing three times with 8 ml distilled hexane. The weight of triolein recovered was determined after drying in a rotary evaporator. For each SPMD, the concentrations of EDCs of three sub-samples, each containing 60 μl triolein, were analyzed by gas chromatography-mass selective detector (Hewlett Packard 58 Agilent Technologies 7890A GC System 90 series II, equipped with Agilent Technologies 5975C Inert XL MD triple-Axis mass selective detector; Column: HP-5MS column, 30 m × 0.32 mm × 0.25 μm film thickness, 95% dimethyl-5% diphenyl-polysilohexane; Temperature program: 70 °C for 2 min, then increasing by 12 °C min^{-1} to 260 °C for 15 min; Injector and detector: 270 °C; Split ratio: 10:1) (Briciu et al., 2009; Richardson et al., 2003). The sub-samples were spiked with 10 μl of an internal standard mixture working solution comprised of 3 μg ml^{-1} decachlorobiphenyl and 5 μg ml^{-1} m-terphenyl. The percent recoveries were 87.4% for 4-NP, 78.9% for TCS, 82.3% for BPA, 75.6% for E2 and 74.7% for EE2. The reported concentrations of EDCs were not corrected for recovery.

2.3. Analysis of heavy metals

Concentrations of six heavy metals (Cd, Cr, Cu, Hg, Pb and Zn) in each AM were determined, following the methods described in Wu et al. (2007). Briefly, the resins in each AM were emptied onto a sintered glass filter and rinsed several times with Milli-Q water. Elution of the resin was conducted with 6 M nitric acid prepared from 70% Suprapur nitric acid. The elutriate was then diluted with Milli-Q water to a known volume. Inductively coupled plasma atomic emission spectroscopy (Optima 2100, Perkin Elmer Instruments, USA) was used to determine the concentrations of heavy metals and results were expressed as mg g^{-1} resin.

Table 1
Characteristics of the three sewage treatment plants (STPs) selected for the present study.
(Data obtained from the Drainage Services Department, Hong Kong SAR government).

	Cheung Chau	Stonecutters Island	Shatin
Treatment method	Primary treatment	Chemically enhanced primary treatment (CEPT)	Secondary treatment using activated sludge
Population served	23,000	3.5 million	0.6 million
Average flow rate	12,000 m^3 day^{-1}	1.4 million m^3 day^{-1}	0.23 million m^3 day^{-1}
Hydraulic retention time	1.5 h	1.5 h	20 h
Removal efficiencies of total suspended solids (TSS) and biochemical oxygen demand (BOD)	TSS: 70% BOD: 30%	TSS: 80% BOD: 60%	TSS: >90% BOD: >90%

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