Science of the Total Environment 575 (2017) 588–594

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

A simple model for estimating the concentrations of natural estrogens in raw wastewater

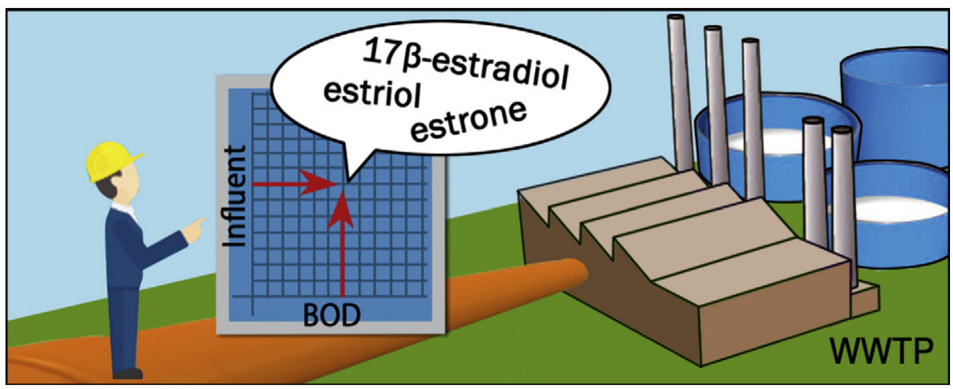
Pniela Dotan [a], Alon Tal [b], Shai Arnon [a,*]

[a] Zuckerberg Institute for Water Research, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boqer 84990, Israel
[b] Swiss Institute for Dryland Environmental and Energy Research, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boqer Campus, 84990, Israel

HIGHLIGHTS

- A model for evaluating natural estrogen concentrations in raw sewage was developed.
- Results are based on a linear regression using data from 61 wastewater treatment plants.
- An association between BOD and natural estrogen loads was identified.
- This paper compares the predictions and errors of our analysis to previous studies.
- The model can assist in predicting the fate of natural estrogens during treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form 31 August 2016
Accepted 2 September 2016
Available online 9 September 2016

Editor: Jay Gan

Keywords:
Natural estrogens
Wastewater treatment plant
Model
Biochemical oxygen demand (BOD)

ABSTRACT

This study provides a tool for predicting the concentrations of the natural estrogens (NEs) estrone, 17β-estradiol and estriol in raw wastewater (WW). Data characterizing the biochemical oxygen demand (BOD), NE concentrations, and discharges of raw sewage to wastewater treatment plants (WWTPs) were collected from various publications and used in the model formulation. A strong correlation was found between the log transformed BOD and the log transformed estrone load ($r^2 = 0.84$, $n = 61$), the log transformed 17β-estradiol load ($r^2 = 0.89$, $n = 52$) and the log transformed estriol load ($r^2 = 0.80$, $n = 40$). The models are reasonably accurate when compared to the measured concentrations and slightly better than previous modeling efforts. The relative amounts of data falling within ±50% error were 67% for estrone, 63% for 17β-estradiol, and 55% for estriol. Because the model was developed from a wide array of WWTPs from five continents, it is universal and can be used for projecting concentrations of NEs from a wide range of mixed domestic and industrial sources, but may be less precise when sources contain high levels of NEs or BOD (e.g., WW from dairy farms and food processing plants). The model is expected to improve our ability to predict the fate of NEs in WWTPs and in the receiving environment, which currently relies on estimating the concentrations of NEs in raw wastewater. Its application is especially valuable since direct measurement of NEs in raw WW is expensive and practically impossible in many developing countries due to the lack of expertise and funds.

* Corresponding author.
E-mail address: sarnon@bgu.ac.il (S. Arnon).

http://dx.doi.org/10.1016/j.scitotenv.2016.09.015

1. Introduction

Endocrine-disrupting chemicals (EDCs) are a subgroup of micro-pollutants that have become a major environmental concern in aquatic systems due to their potential harmful effects to aquatic organisms (Futran Fuhrman et al., 2015; Luo et al., 2014; Gunnarsson et al., 2009; Caldwell et al., 2012). EDCs include a wide range of chemicals, but one of the most potent groups is composed of natural estrogens (NEs), in particular, estrone, 17β-estradiol and estriol (Gross-Sorokin et al., 2005). The aforementioned NEs are naturally produced and secreted by humans and animals; therefore, they are extremely common in domestic and dairy farm WW (Hanselman et al., 2003; Lintelmann et al., 2003; Zheng et al., 2008), in treated municipal WW, as well as in the receiving environment (Manickum and John, 2013; Luo et al., 2014).

Evaluating the fate of NEs in wastewater treatment plants (WWTPs) will enable the prediction of environmental NE concentrations in aquatic systems and the potential risk they pose to aquatic organisms (Luo et al., 2014; Johnson and Williams, 2004; Thompson et al., 2011; Bertin et al., 2009). Direct measurements are one option for evaluating the levels of and risks from NEs·These measurements, however, are complicated and expensive and, thus, typically not incorporated as part of a standard analysis in WWTPs and environmental systems even in most developed countries. Relying on modeling offers another method for estimating the potential risk from NEs, and has been used in numerous studies during the last decade (Johnson and Williams, 2004; Kostich et al., 2013; Pomiès et al., 2012; Thompson et al., 2011; Liu et al., 2015). Modeling is potentially low cost and provides high temporal resolution. In addition, model estimation strongly relies on the level of accuracy of the predicted NE concentrations in the incoming raw WW.

Various models were developed over the years to predict the NE concentrations in raw WW. Johnson et al. (2000) developed a model that predicts the influent NE concentrations (estrone, 17β-estradiol, and estriol) and 17α-ethiniylestradiol by summing the estrogens excreted in urine from different groups of the contributing human population. This model was revised by Johnson and Williams (2004) by incorporating human urine and fecal excretion, including conjugation and metabolism of these compounds by different members of the population. The latter model also includes the loss of estrogens through transport in sewer networks, while taking into account transformation products. Kostich et al. (2013) established another model by using a similar approach, which is based on the data of raw WW flow rates relative to population, local demographics, and estrogen excretion rates. The latter model refines the reported NE excretion rates for different demographic groups by meta-analysis of published data.

One of the major drawbacks of the aforementioned modeling approaches lies in the detailed demographic information required. For example, the distribution by age and gender, the specific diet and race of the population, the number of pregnant women in the population, and the retention time of WW in network sewerage should be well-characterized. These kinds of data are dynamic over time, and their collection requires access to a reliable and recent census, which often is either not available or lacks the necessary resolution. The fact that substantial conjugation of the NEs may occur in wastewater poses an additional challenge to predicting their concentrations in raw wastewater as was recently shown by Liu et al. (2015). Other modeling approaches focus on the fate of organic contaminants in WWTPs based on information about the governing processes (e.g., sorption and degradation). The latter requires information that can be found in the literature (e.g., reaction rates and sorption constants) and information regarding the NE concentrations in the raw WW (Pomiès et al., 2012).

Another approach for evaluating the NE concentrations in raw WW was introduced by Drewes et al. (2005). Drewes et al. found a positive linear correlation between the loads of NE (measured indirectly by the *E*-Screen method) and biochemical oxygen demand (BOD) in raw WW from seven WWTPs in the USA. For example, the regression between BOD and 17β-estradiol and estriol was found to be high with $r^2 = 0.92$. Despite the fact that this approach offers little insight into the mechanisms and biological processes underlying the NE concentrations, it does provide the advantages of simplicity and the relative availability of relevant information. Observations by Drewes et al. (2005) led us to the hypothesis that there is a universal correlation between WW composition ("strength") and NE in raw WW. To test this hypothesis, we reviewed the literature and conducted a regression analysis to search for correlations between the concentrations and loads of the NEs estrone, 17β-estradiol and estriol and WW strength parametrization, such as the load of BOD, the chemical oxygen demand (COD), total suspended solids (TSS), and NH_4^+. The ultimate goal of this parametrization was to develop a model for predicting the NE concentrations in raw WW.

2. Materials and methods

2.1. Data collection

Data were collected from peer-reviewed publications on NEs in WWTPs from the years 2000–2016. Relevant data that were searched included: influent concentrations of estrone, 17β-estradiol, estriol, BOD, COD, TSS, NH_4^+, and WW flow. NE concentrations were only archived if a direct chemical analysis was done because many studies used indirect quantification methods, such as bioassays (Avberšek et al., 2013; Nelson et al., 2007). We found only nine publications that reported all the aforementioned data in a numerical format. In order to expand our database, data that appeared only in graphs from two additional publications were added by obtaining the values after extraction with WebPlotDigitizer (http://arohatgi.info/WebPlotDigitizer/app/, 2015). WebPlotDigitizer was evaluated by Kadic et al. (2016) and found to be a reliable and accurate tool for extracting values from graphs, with an interclass correlation coefficient (ICC) above 0.92 (An ICC above 0.75 is considered to show good reliability (Portne and Watkins, 2000)).

2.2. Data analysis

Data combining the flow and concentrations were used to calculate the loads of BOD, estrone, 17β-estradiol and estriol in raw WW following Eq. (1).

$$M = Q * C \tag{1}$$

where M is the daily load (mass/time), Q is the flow rate (volume/time) and C is the average concentration (mass/volume).

A linear regression analysis was conducted to analyze the individual correlations between the loads of BOD and those of estrone, 17β-estradiol and estriol. The entire database was log transformed because the distribution violated the assumptions of the residuals' normality and homogeneity. Data that fell outside of the 95% confidence interval are shown but not included in the regression analysis and model formulation. In addition, in order to broaden the analysis, our literature review also contained information on the COD, TSS, and NH_4^+ concentrations in WWTPs. However, fewer data points were available in conjunction with NE concentrations, and a detailed analysis could not be conducted and compared with that of BOD.

After obtaining the correlation data, the linear fit was used to evaluate the validity and usefulness of the model by calculating a predictive concentration for each one of the NEs that appeared in the database. The differences between the measured and the predicted values of estrone, 17β-estradiol and estriol were evaluated by applying Eq. (2) to each one of the values.

$$Error\ (\%) = \frac{C_{measured} - C_{predicted}}{C_{measured}} * 100 \tag{2}$$

where E is the estimated error (%) of the model, $C_{measured}$ is the measured concentration of estrone, 17β-estradiol or estriol (ng/l), and