Occurrence and fate of endocrine disrupting compounds in wastewater treatment plants in Israel and the Palestinian West Bank

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HIGHLIGHTS

- Hormone concentrations were higher in the Palestinian than in the Israeli WWTPs.
- EDC removal in this study was higher than the reported values around the world.
- Triclosan removal can be improved in secondary treatment by increasing HRT.

ARTICLE INFO

ABSTRACT

Israel and its Palestinian neighbors constitute a unique venue for evaluating the treatment efficiency and potential environmental risks of endocrine disrupting compounds (EDCs) in wastewater treatment plants (WWTPs), because of their physical proximity yet contrasting societal dynamics. Israel primarily relies on advanced tertiary sewage treatment and recycles over 85% of its treated wastewater, while in the Palestinian Authority (PA), there is only secondary treatment levels at WWTPs and reuse is minimal (<1%). To evaluate the extent of EDC occurrence and treatment efficiency, we conducted four sampling campaigns over two consecutive years, and measured the concentrations of selected EDCs in raw wastewater (WW), treated WW and sludge in six WWTPs in Israel, as well as in two Palestinian plants. Low concentrations of bisphenol A, octylphenol and triclosan measured in the raw WW in the Palestinian WWTPs reflected the relatively modest industrial activity and consumption habits as compared to the westernized consumer patterns in Israel. On the other hand, hormone concentrations in raw WW were higher in the Palestinian WWTPs than those in the Israeli WWTPs, presumably because of a dilution effect associated with a higher water per capita consumption among Israelis. Despite these differences in raw WW concentrations, the removal efficiency in all advanced WWTPs was relatively high when compared to averages reported internationally.

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1. Introduction

Endocrine disrupting compounds (EDCs) are a sub-group of micropollutants that may alter the hormonal functioning of the endocrine system in humans and wildlife (Cwiertny et al., 2014). Varying concentrations of EDCs have been found in different aquatic systems around the world (Vidal-Dorsch et al., 2012; Xu et al., 2011). EDCs are introduced to the aquatic environment through various pathways including the direct discharge of raw or treated wastewater (WW) from wastewater treatment plants (WWTPs), the application of treated sludge, runoff from agricultural and industrial areas, and via irrigation with treated WW (Hamid and Eskicioglu, 2012). WWTPs are of particular interest because they continuously discharge EDCs into the environment, but at the same time, can significantly reduce EDC loadings through

effective treatment (Drewes et al., 2005).

The reduction in EDC concentrations during WW treatment, without identifying specific elimination mechanisms, is often referred to as removal (Stadler et al., 2012). EDCs can be removed from wastewater by physical, chemical and biological processes, depending on the characteristics of the compounds and the conditions during the treatment (Hamid and Eskicioglu, 2012; Ifelebuegu, 2011). The concentrations of EDCs in raw and treated WW also depend on the socioeconomic composition of the contributing society, which is reflected, for example, by the levels of industrial development and agricultural practices (Schwarzenbach et al., 2006). Extensive WW reuse can also affect the distribution of EDCs in the environment since, in many cases, EDCs were identified in treated WW. For example, in more humid regions, treated WW is discharged into rivers, posing a risk to ecosystems (Meybeck et al., 1996; Drechsel et al., 2010). In semi-arid and arid environments, such as the Middle East, treated WW is primarily reused for irrigation and can find its way into food (Malchi et al., 2014) or can be leached toward the groundwater (Avisar et al., 2009).

Israel (IL) and the Palestinian Authority (PA) share the same geographic province in the central part of the Middle East, and most of the catchments in this area are transboundary. However, their water treatment and reuse profiles differ significantly, with little cooperation taking place between the two sides, even in cases where raw or treated sewage is leached between the two territories (Al-Sa'ed and Tomaleh, 2012; Palestinian Water Authority, 2012). In Israel for example, over 90% of the WW is treated and 86% of the treated WW is reused for irrigation, while a small fraction is discharged into the aquatic environment (Israel Water Authority, 2015). In the Palestinian West Bank, there are only two advanced functioning WWTPs that serve 20—35% of the households with almost no reuse (Al-Sa'ed and Tomaleh, 2012). While the above-mentioned WWTPs in the Palestinian West Bank employ only secondary treatment, tertiary treatment is becoming standard among Israeli WWTPs due to regulatory requirements (Israel ministry of enivronmental protection, 2010). Despite the fact that Israel's wastewater treatment standards are relatively new (from the year 2010), no regulation exists in Israel (nor in the world) for EDCs, and there is a clear shortage of information about EDCs and other trace organic compound occurrences in the Middle East (e.g., Alidina et al., 2014).

To evaluate the extent of EDC occurrence in WWTPs in Israel and the West Bank of the Palestinian Authority, we measured the concentrations of selected EDCs in raw WW, treated WW and sludge in eight WWTPs. The main objectives of this research were to evaluate the removal efficiency of EDCs in different treatment technologies and operating conditions (including the level of treatment), along with the associated risks from treated WW in contiguous countries with such dramatically distinct socioeconomic conditions.

2. Materials and methods

2.1. Study sites

Eight WWTPs were selected for the current study, including six in Israel and two in the PA. Despite efforts made to sample a greater number of WWTPs in the West Bank in the PA, none of the other facilities operated continuously during the study. Details on the technology, treatment levels, hydraulic retention time (HRT) during the secondary treatment, and reuse in the WWTPs are summarized in Table 1.

2.2. Water and sludge sampling

Four sampling campaigns were conducted during the winters and summers of 2013—2014. Raw, secondary and tertiary (where relevant) WW and sludge were sampled in each WWTP. Composite samples of raw and secondary-treated wastewater were obtained over a 24-h period by using automatic samplers (ISCO 3800 and global water WS1700), equipped with 4-L dark glass bottles that were kept on ice. Raw wastewater samples were taken after grit removal. Tertiary level samples were taken as grab from reservoirs, where the water is well-mixed and residence time is greater than 24 hours. Sodium sulfite was added to all water samples in order to neutralize chlorine residues, and the samples were acidified to a pH of 2 using 6 N HCl to prevent microbial activity. Sludge samples were taken in each WWTP using 120-ml glass containers. All samples were stored at 4 °C until transported to the laboratory (<24 h). Water samples were kept in the laboratory at 4 °C until extraction (<14 days), and sludge samples were frozen at −20 °C until extraction (<1 year).

2.3. Sample preparation and analysis

2.3.1. WW sample preparation and analysis

The target compounds assessed in this study included estriol, estrone, 17-β estradiol, testosterone (TST), bisphenol A (BPA), octylphenol (OP), triclosan (TCS), nonylphenol (NP) and atrazine. These compounds are either produced naturally (e.g., hormones) or are commonly used in Israel and the PA. The compounds were extracted from the WW using the solid phase extraction (SPE) technique. EDCs (except for TCS) were extracted according to EPA 539 protocol (USEPA, 2010), while TCS extraction was conducted according to EPA 525.2 protocol (Eicheelberger et al., 1995). SPE was conducted using Empore C_{18} extraction disks. The final extracts were stored at −20 °C until analysis (<90 days). The analysis of TCS was done by GCMS (TRACE GC2000/FINNIGAN POLARIS MS, ThermoQuest, USA) equipped with an Rxi®-5Sil MS column (Restek, Bellefonte, PA, USA), 30 m × 0.25 mmID × 0.25 μm, and an ion trap mass spectrometer (FINNIGAN POLARIS/GCQ plus). Analysis of EDCs was conducted with ES- LCMSMS (Waters Xevo TQS, Waters Corporation, USA) and Acquity. A 1.7 μm 2.1 × 50 mm column was used for separation. The minimum quantification limit (MQL) of each compound is given in Table S1 (Supplementary information).

2.3.2. Quality Assurance/Quality Control

A Quality Assurance/Quality Control protocol was carried out during the sampling and sample preparation. Laboratory and field blanks, as well as laboratory fortification blanks and matrices (spiked blanks and samples), were used in each batch of samples. Target compounds were identified by comparing either retention times and the full mass spectrum (EPA 525.2) or 2—3 multiple reaction monitoring (MRM) transitions (EPA539) of the substance in the sample and its authentic standard, which were tested under the same conditions. Concentrations of EDCs were calculated using a standard internal calibration procedure. Internal standards were used for the following compounds: phenanthrene D_{10}, BPA-D_{16}, estradiol $^{13}C_6$, estriol $^{13}C_3$, estrone $^{13}C_6$, and testosterone D_5. Analytical standards were purchased from Sigma-Aldrich. Analytical grade reagents for extractions and instrumental analysis (methanol, ethyl acetate, methylene chloride, sodium sulfate, hydrochloric acid, ammonium acetate) were all purchased from either Sigma-Aldrich or J.B. Baker.

The MQL was evaluated separately for each compound during initial validation of the analytical methods. Spiked samples were treated according to the procedure described above, and were used to create the calibration curves. The accuracy and precision of the