Environmental Pollution 178 (2013) 271–277

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

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

Comparing predicted estrogen concentrations with measurements in US waters

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ARTICLE INFO

Article history:
Received 19 December 2012
Received in revised form
7 March 2013
Accepted 12 March 2013

Keywords:
Estrogens
Estradiol
Wastewater
Aquatic
Water

ABSTRACT

The range of exposure rates to the steroidal estrogens estrone (E1), beta-estradiol (E2), estriol (E3), and ethinyl estradiol (EE2) in the aquatic environment was investigated by modeling estrogen introduction via municipal wastewater from sewage plants across the US. Model predictions were compared to published measured concentrations. Predictions were congruent with most of the measurements, but a few measurements of E2 and EE2 exceed those that would be expected from the model, despite very conservative model assumptions of no degradation or in-stream dilution. Although some extreme measurements for EE2 may reflect analytical artifacts, remaining data suggest concentrations of E2 and EE2 may reach twice the 99th percentile predicted from the model. The model and bulk of the measurement data both suggest that cumulative exposure rates to humans are consistently low relative to effect levels, but also suggest that fish exposures to E1, E2, and EE2 sometimes substantially exceed chronic no-effect levels.

1. Introduction

Estrogenic contaminants in water are suspected of causing adverse reproductive effects in humans (reviewed in Toppari et al., 1996) and aquatic life (reviewed in Matthiessen and Sumpter, 1998). A major source of these contaminants is thought to be municipal wastewater (reviewed in Gross-Sorokin et al., 2006), where most estrogenic activity is typically accounted for by the steroidal estrogens (SEs) estrone (E1), beta-estradiol (E2), estriol (E3), and ethinyl estradiol (EE2).

In order to better understand the sources and spatial distribution of SEs, a watershed-level model of municipally derived SEs has been proposed (Johnson and Willams, 1999; Johnson et al., 2000; Johnson and Williams, 2004). This model considers local population size, SE excretion by different demographic segments, national demographic proportions, local wastewater production rates, estimates of SE removal rates in the wastewater treatment plant (WWTP), and in-stream dilution of WWTP effluent. The model fits measurement data for the study area fairly well, although some unexpectedly high measured in-stream concentrations were noted. The mismatch was attributed to uncertainties and unaccounted for variability in model parameters, such as excretion, removal, and dilution rates. Subsequent studies used similar models and the same excretion parameters to model SEs in other watersheds (Sumpter et al., 2006; Jobling et al., 2006; Bertin et al., 2009; Balaam et al., 2010) or in-stream concentrations on a nationwide basis (Williams et al., 2009; Hannah et al., 2009; Anderson et al., 2012). Generally, a reasonable fit between model predictions and measured concentrations has been reported. Nevertheless, some measurements greatly exceeding model predictions have been noted. It has been suggested that these discrepancies arise from matrix interference resulting in analyte misidentification or unreliable quantification (Hannah et al., 2009).

Studies have differed somewhat in their conclusions about fish health. Some (Hannah et al., 2009; Anderson et al., 2012) emphasize that the bulk of exposure scenarios considered appear to result in exposure rates well below estimated effect levels for humans and fish. Other researchers have focused more on evidence suggesting SEs as likely contributors to reproductive impairments, at least for some local fish populations (Sumpter et al., 2006; Jobling et al., 2006; Bertin et al., 2009; Balaam et al., 2010). To some extent this

List of abbreviations: CWNS, Clean Watersheds Needs Survey; E1, estrone; E2, 17-beta-estradiol; E3, estriol; EE2, 17-alpha-ethinyl estradiol; L, liters; LOEC, lowest observable effect concentration; MEC, measured environmental concentration; MRL, method reporting limit; ng, nanograms; PEC, predicted environmental concentration; PNEC, predicted no-effect concentration; POCIS, Polar organic chemical integrative sampler; SE, steroidal estrogen; WW, wastewater; WWTP, wastewater treatment plant; ZCTA, zip-code tabulation area.

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0269-7491/$ – see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.envpol.2013.03.024

difference may reflect that the more geographically targeted studies chose sites that were suspected of being impacted.

In this study, we attempt to improve model predictions of the upper limits of measured concentrations and investigate factors driving higher concentrations. We refine previously reported SE excretion rates for different demographic segments, based on an updated meta-analysis of the literature. In order to investigate effects on model predictions, we use EE2 consumption rate estimates from published health survey data, rather than commercial marketing data. We use excretion rates for SEs along with local demographic proportions, rather than nationally averaged demographic proportions, and individual WWTP parameters, rather than nationally averaged parameters, to estimate upper limits on SE concentrations in the influent of WWTPs across the US. We then compare the distribution of predicted concentrations to maximum concentrations reported in wastewater and ambient water. Finally, we compare model predictions as well as reported measurements to published effect levels in humans and fish.

2. Materials and methods

2.1. Data analysis

Data analysis was performed using R 2.14.2 (R Development Core Team, 2012), using built-in functions and functions from the standard base packages.

2.2. Estrogen excretion rates

Excretion rates of the natural SEs E1, E2, and E3 were estimated by meta-analysis of published data, which is detailed in Supplement 1. Excretion of EE2 was calculated for users of contraceptive pills, patches, and rings. Pill excretion was assumed to be 50% of an administered dose of 35 ug/day for 21 out of every 28 days (Kostich and Lazorchak, 2008). Excretion from patch users was assumed to be 100% of a 20 ug/day dose for 21 out of 28 days (per Ortho Evra patch prescribing information, downloaded October 19, 2010, from: http://www.orthoevra.com/sites/default/files/assets/OrthoEvraPI_0.pdf). Excretion by ring users was assumed to be 100% of a 15 ug/day dose for 21 out of 28 days (per Nuvaring prescribing information, downloaded October 19, 2010, from: http://www.spfiles.com/pinuvaring.pdf).

2.3. Wastewater plant parameters

The Clean Watershed Needs Survey (CWNS, US EPA, 2004) lists the size of the population served and the flow rate for most WWTPs in the US, as reported by plant operators. These reports occasionally contain typographical errors and frequently contain rough estimates of the size of the population served by the facility. WWTPs listed in CWNS were included if they reportedly served a population greater than 100, at least 75% of their flow was of municipal origin, at least 75% of their served population consisted of local residents, and per capita wastewater production was between 50 and 1000 L per person per day.

CWNS contains state identifiers for all listed WWTPs, geographical coordinates of discharge outfalls for many WWTPs, and zip codes (included as part of the WWTP mailing address) for many WWTPs. When the outfall location was available, the facility was assigned the zip code tabulation area (ZCTA – a geographical unit used to organize census data, which approximates the corresponding postal zip code) corresponding to the closest (distance calculated with haversine formula; Sinnott, 1984) ZCTA centroid within the same state. If outfall location was unavailable, but a mailing address was listed, the mailing zip code was assigned to the facility.

Of the 22 795 discharging facilities listed in CWNS, 12 566 met inclusion criteria listed above and could be assigned a ZCTA. Our distributional analysis is based on these WWTPs, which produce 22.1 billion gallons (83.7 million m^3/d) of wastewater per day (out of a CWNS total of 34.2 billion gallons per day, or 129.5 million m^3/d), and serve 178 339 244 people (out of a CWNS total of 239 749 259 people).

2.4. Local demographics

Census data (Census 2000 Summary File 1, US. Census Bureau, 2001), containing the number of people by sex and age for each zip code tabulation area (ZCTA) was downloaded on October 12, 2010 from http://factfinder.census.gov/servlet/DCGeoSelectServlet. For each of the 12 566 WWTPs (described at the end of the wastewater plant parameters section of the material and methods), the size of the population served was subdivided by sex and age, based on demographic proportions estimated from census data for the corresponding ZCTA. Literature values were adopted for menarche rates (Anderson et al., 2003), pregnancy rates (Ventura et al., 2009), menopause rates (Kato et al., 1998), and hormone replacement therapy (HRT) rates (Hsu et al., 2009). We assumed all abortions or losses occurred at 10 weeks gestation, all deliveries occurred at 40 weeks, and no more than one pregnancy occurred per woman per year. The HRT usage rate was calculated as the geometric mean of figures reported for the periods 1999–2000, and 2003–2004. Half of males aged 10–14 were classified as adults, while the other half were classified as children.

2.5. Modeled SE concentrations

Concentrations of SEs in wastewater influent were estimated for each of the 12 566 WWTPs (described at the end of the wastewater plant parameters section of the material and methods) based on plant flow rates relative to population, local demographics, and estrogen excretion rates. For each plant and individual SE, the number of people in each demographic group was multiplied by that SE's daily excretion rate for that demographic group, and then summed across demographic groups yielding an estimate of the total daily load (in mass units) of each SE entering that particular plant. The influent concentration for the WWTP was then estimated as the SE load divided by the total daily flow rate for that plant. In order to account for fluctuations due to temporal variability in influent composition, predicted means were multiplied by the adjustment factor 1.4 to account for temporal within-plant variation. This adjustment factor was adapted from the only study we know of in the US (Filali-Meknassi et al., 2007) examining within-plant variations in influent concentrations of E1 and E2.

2.6. Comparison to MECs

Peer reviewed publications reporting MECs for E1, E2, E3, or EE2 measured within the US were identified via literature search. Studies were included if they were conducted in the US, and were published between January 1999 and January 2010. Measurements from wastewater, surface water, and ground water were included. MECs from hospital effluents and treated drinking water were excluded. Polar organic chemical integrative sampler (POCIS) data were excluded. Non-detections and detections that could not be quantified were recoded as half the method reporting limit (MRL), unless the MRL was greater than the 10th percentile of the maxima from other studies for that analyte in that medium (suggesting an unusually high MRL), in which case the non-detect data was excluded from the analysis. For comparisons to the modeled concentrations, measured concentrations of SE conjugates (glucuronides and sulfates) were added to the measured parent concentration on an equimolar basis.

3. Results and discussion

3.1. Estrogen excretion rates

We found 36 published studies reporting human excretion rates for E1, E2, or E3. A summary of the results of a meta-analysis of these data is presented in Table 1, the study-level data are tabulated in Supplement 2, and meta-analysis forest plots are provided in Supplement 3. Scant or no data was available for some demographic groups (See Tables A and B in Supplement 2). In particular, we found no fecal excretion data for children of either sex or for menstruating women during the luteal period, early pregnancy, or mid-pregnancy. We also found no urinary excretion data for E3 in post-menopausal women taking HRT. The missing data were imputed, as described in Supplement 1.

Our estimates for E1 as well as E2 fall within ranges of previously reported estimates (Johnson and Williams, 2004; Hannah et al., 2009; Anderson et al., 2012), except E2 excretion in menstruating women was about 50% higher, and excretion of E1

Table 1
Excretion rate parameters from meta-analysis, expressed in micrograms per day. Contraceptive users were also counted as menstruating women.

	E1	E2	E3	EE2
Adult male	3.51	1.83	3.21	0
Female child	0.595	2.50	0.918	0
Male child	0.629	0.54	0.731	0
Menstruating woman	9.32	6.14	17.4	0
Pregnant woman	787	277	9850	0
Menopausal, no HRT	2.93	1.49	3.90	0
Menopausal, with HRT	31.5	59.2	90.7	0
Contraceptive Pill	0	0	0	13.1
Contraceptive Patch	0	0	0	15.0
Contraceptive Ring	0	0	0	11.3