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Seasonal variations of steroid hormones released by wastewater treatment plants to river water and sediments: Distribution between particulate and dissolved phases

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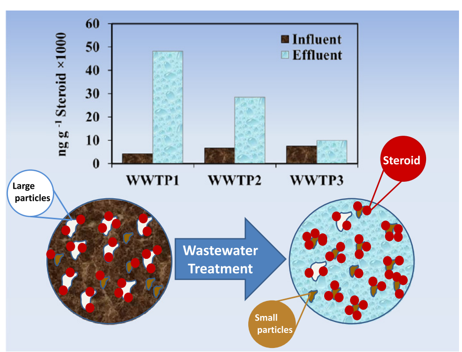
HIGHLIGHTS

- Environmental levels of steroids were determined in dissolved and particulate phases.
- Extensive amounts of steroids detected in suspended particles and sediment.
- Steroids in drinking water intakes were at the same level as treated sewage.
- Biological refractory steroids may accumulate in drinking water plant sludge.

GRAPHICAL ABSTRACT



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ABSTRACT

Extensive environmental monitoring was conducted in an urban river impacted by multiple combined sewer overflows (CSOs) and wastewater treatment plant (WWTP) discharge points. Temporal and spatial distributions of dissolved and particulate steroids (progesterone (Prog), testosterone (Testo), medroxyprogesterone (MDRXY-Prog), levonorgestrel (Levo), norethindrone (Nore), estrone (E1), estradiol (E2), estriol (E3), and 17α-ethinylestradiol (EE2)) were investigated in sewage, WWTP effluents, receiving river water and sediments, and in drinking water plant (DWP) intakes. Steroids were detected in both dissolved and particulate phases with mean concentrations from 21 ng L^{-1} to 389 ng L^{-1} in raw sewage and from 10 ng L^{-1} to 296 ng L^{-1} in treated wastewater. The particle-associated steroids represented 0–82% of their total concentration as some steroids like E1 and E3 were detected only in the dissolved phase while MDRXY-Prog (81%), Nore (71%), and EE2 (>75%) were primarily detected in the particulate phase. Particle-associated steroids were detected in spring samples from river water with mean concentrations ranging from 5.4 ng L^{-1} to 35.7 ng L^{-1} compare to 3 ng L^{-1} to 6.8 ng L^{-1} in summer samples. Levels of particle-associated Testo, Nore, E2 and Levo in DWP intakes (406.2–13,149.1 ng g^{-1}) were similar to those found in raw sewage (336.6–7628.8 ng g^{-1}), indicating their persistence in the suspended phase from discharge points. Total steroids measured in sediments were in the range of 7–1213 ng g^{-1}, 5–25 ng g^{-1}, and 22–226 ng g^{-1} in autumn, spring, and summer, respectively.
Our findings confirm the presence and seasonal variation of a mixture of particle-associated steroids in drinking water sources. The presence of high concentrations of a mixture of particle-associated steroids in DWP intakes

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highlight the need for highly effective particle-removal processes to eliminate these recalcitrant compounds during drinking water production. Finally, the detected concentrations raise concerns about their potential environmental effects.

1. Introduction

Steroid hormones are ubiquitous in aquatic environments at trace concentrations ranging from a few ng L^{-1} to μg L^{-1} (Gorga et al., 2015; Fent, 2015; Chang et al., 2011). Negative effects of steroid hormones on aquatic organisms such as sexual disorders, feminization, masculinization, and infertility have been confirmed by several studies (Milla et al., 2011; Lange et al., 2001; Lai et al., 2002). When assessing the occurrence and fate of steroid hormones in drinking water sources, it is important to consider all environmental components of both the dissolved and particulate phases of hormones: WWTP discharges, CSOs, river water and sediments. Sorption onto solids and biological degradation are two main pathways for the removal of steroids from the aqueous phase. Steroid hormones are non-polar hydrophobic compounds that can be easily adsorbed onto river sediments. Sorption of steroids on aquatic sediments can directly affect their mobility, transformation, bioavailability and subsequent fate in the natural water systems including drinking water intakes (Yu et al., 2004; Yamamoto et al., 2003; Ying et al., 2003; Sun et al., 2012). The relative loads of dissolved and particulate fractions of some steroids have been assessed in raw sewage and treated wastewater (WW) (Andrasi et al., 2013) and to a lesser extent in river water (Gong et al., 2016; Labadie and Budzinski, 2005). In Southwestern France, some dissolved estrogens were systematically detected in a WWTP effluent (17–71 ng L^{-1} E1, <1.0–4.4 ng L^{-1} E2, <1.0 ng L^{-1} EE2) but without any clear seasonal trends. However, no steroids were detected in the particulate phase (≥0.7 μm) of the WWTP effluent presumably because of the low suspended particle concentration (50 mg L^{-1}) with 30% carbon content (Labadie and Budzinski, 2005). Based on an overview of recent studies, the final concentration of steroids in WWTP effluent depends on the efficiency of the applied processes that reduce the amount of suspended particles in the effluent (Andrasi et al., 2013; Gong et al., 2016; Labadie and Budzinski, 2005; Svenson et al., 2003; Dagnino et al., 2010). Activated sludge and waste stabilizing ponds provide higher removal efficiencies of estrogenic activity and estrogens removals (Nie et al., 2012). In contrast, trickling filters were found to be less effective processes to remove suspended particles because of short sludge retention times (Dagnino et al., 2010). Degradation accounted for 78–99% and 73–96% of the removal of estrogens and progestogens from aerobic and anaerobic tanks with total concentrations in raw sewage up to 102 and 57 ng L^{-1} (Fan et al., 2011). Seasonal variations can directly affect the fate of steroids in both dissolved and particulate phases. The fluctuation of E1 and E2 levels between raw sewage and effluent was found to be highly temperature dependent (Nie et al., 2012). The concentrations of both compounds in the effluent in summer at 27 °C were up to 30 fold higher than that in the effluent during spring and winter (12–19 °C). Additionally, biological processes were more effective during the warmer temperatures as microbial degradation of estrogens increases with higher temperatures (75.4% removal for E3 and >90% for other estrogens). Likewise, lower steroid levels have been detected in sediments during warmer months most likely due to a higher biodegradation rates at higher temperatures (López de Alda et al., 2002; Jurgens et al., 1999).

The fate of mixtures of estrogens, progestogens and androgens from their urban discharge sources (WWTPs and CSOs) to the surface water intakes of DWP is poorly documented in terms of persistence and partitioning (dissolved versus particulate phases). Estrogens were detected in the dissolved phase of samples taken downstream of WWTPs in southern Australia with mean concentrations of 4.49, 0.93, and 0.05 ng L^{-1} for E1, E2, and EE2, respectively (Ying et al., 2009). Higher levels of estrogens were potentially related to colder weather and higher rainfall that led to increased loads of estrogens from agricultural lands and animal farms. Although estrogens are the most frequently detected steroids in surface waters, relatively higher concentrations of progestogens and androgens have been reported compared to estrogens (Chang et al., 2011, 2009; Kolpin et al., 2002). Testo was found in 42% of samples from four rivers in Beijing, China with a maximum concentration of 8.6 ng L^{-1}; Prog was found in 93% of samples with a peak concentration of 199 ng L^{-1} (Chang et al., 2009). Given the relatively low partitioning coefficients of steroid hormones with octanol/water partitioning coefficients (log K_{ow}) mostly between 3 and 6; river sediments likely act as environmental sink for these compounds. According to previous studies on the fate of estrogens in river beds, between 13% to 92% of estrogens ended up in the river sediments during the first hours of discharge to the river (Jurgens et al., 1999; Lai et al., 2000). From the various steroid hormones investigated in several studies, E1, EE2, and Nore were the most frequently detected steroids in sediments (López de Alda et al., 2002). The average concentration of steroids in river sediments from Spain increased from 0.51 ng g^{-1} in summer to 4.43 ng g^{-1} in winter and spring (López de Alda et al., 2002).

Prior studies on particle-associated steroids have focused on their occurrence in sediment or wastewater particles and their potential endocrine disrupting effect on aquatic life. Earlier studies concluded that particle-associated steroids had a much lower potential impact on aquatic life (particle phase estrogenicity was <0.1 ng L^{-1}) as compared to the dissolved phase (dissolved phase estrogenicity decreased from 4.5 to 1.4 ng L^{-1} from raw sewage to effluent) (Svenson et al., 2003), while more recent studies report significant negative effects of sediment and wastewater particle-associated steroids (Dagnino et al., 2010; Sangster et al., 2016; Jessick et al., 2014; Kolok et al., 2007; Duong et al., 2010). Smaller particles like clay (>1 μm up to 2 μm) and colloids (<1 μm) are considered to be a more effective sorbent than larger particles (Duong et al., 2010; Sangster et al., 2015; Qi et al., 2014). In one study, the change of the estrogenic activity of E2 was evaluated by sorption on different fractions of sediment particles (Duong et al., 2010). The authors reported that E1, E2, and EE2 interacted more with smaller particles (<1 μm) compared to amount of estrogens sorbed to particles >1 μm up to 50 μm. Their results are in accordance with other studies which also reported higher sorption of Testo, Prog, and estrogens to small soil particles (<2 μm) (Qi et al., 2014) and sediment particles (0.87–1.43 μm) (Sangster et al., 2015). Over 60% of sediment-associated Prog was found attached to fine particles and caused masculinization in fathead minnows exposed to 10 and 100 ng L^{-1} of this compound for 21 days (Sangster et al., 2016). Therefore, the importance of sediment-associated steroids on the fate and the subsequent bioavailability needs to be considered along with their dissolved fraction which has already been well documented.

The primary objective of this work was to document the fate of particle-associated steroids from their discharge points to DWP intakes located on an urban river subject to multiple CSOs and WWTP discharges. Specific objectives included: (1) quantifying the partitioning of steroids in the incoming sewage and effluent of three WWTPs; (2) monitoring the seasonal variation of the particle-associated steroids in the suspended solids and sediments along a 42 km river; (3) quantifying the accumulation of particle-associated steroids in drinking water sludge.