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Review

Dissolved organic matter and estrogen interactions regulate estrogen removal in the aqueous environment: A review

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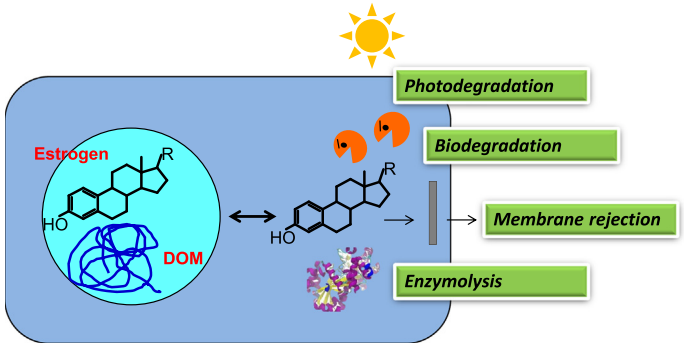
HIGHLIGHTS

- Dissolved organic matter interacts with estrogens via binding or sorption.
- Binding mechanisms include π-π electron donor-acceptor interaction and hydrogen bonding.
- The interactions were primarily associated with dissolved organic carbon quality.
- Methods to characterize and quantify binding or sorption affinity were summarized.
- The regulatory effects of dissolved organic matter on estrogen elimination were discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

This review summarizes the characterization and quantification of interactions between dissolved organic matter (DOM) and estrogens as well as the effects of DOM on aquatic estrogen removal. DOM interacts with estrogens via binding or sorption mechanisms like π-π interaction and hydrogen bonding. The binding affinity is evaluated in terms of organic-carbon-normalized sorption coefficient (Log K_{OC}) which varies with types and composition of DOM. DOM has been suggested to be a more efficient sorbent compared with other matrices, such as suspended particulate matter, sediment and soil; likely associated with its large surface area and concentrated carbon content. As a photosensitizer, DOM enhanced estrogen photodegradation when the concentration of DOM was below a threshold value, and when above, the acceleration effect was not observed. DOM played a dual role in affecting biodegradation of estrogens depending on the recalcitrance of the DOM and the nutrition status of the degraders. DOM also acted as an electron shuttle (redox mediator) mediating the degradation of estrogens. DOM hindered enzyme-catalyzed removal of estrogens while enhanced their transformation during the simultaneous photo-enzymatic process. Membrane rejection of estrogens was pronounced for hydrophobic DOM with high aromaticity and phenolic moiety content. Elimination of estrogens via photolysis, biodegradation, enzymolysis and membrane rejection in the presence of DOM is initiated by sorption, accentuating the role of DOM as a mediator in regulating aquatic estrogen removal.

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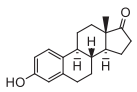
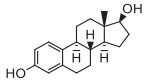
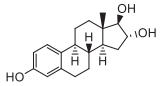
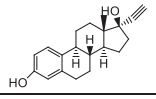
Contents

1. Introduction

Endocrine disrupting compounds (EDCs) are chemicals that exert adverse effects on endocrine systems of humans and wildlife. EDCs include but are not limited to pharmaceuticals, pesticides and hormones, natural or synthetic, among which, estrogens stand out due to their negative effects on aquatic organisms at environmentally-relevant (ng L^{-1}) levels. For example, the lowest observed effective concentration for the synthetic estrogen 17α-ethynylestradiol (EE2) to induce plasma vitellogenin (female yolk precursor protein) in male fathead minnow (*Pimephales promelas*) was 1 ng L^{-1} (Pawlowski et al., 2004; Zhu et al., 2004). The threshed concentration for 17β-estradiol (E2) to induce vitellogenin on female juvenile rainbow trout was 4.7 and 7.9 ng L^{-1} (Thorpe et al., 2001). Exposure to 10 ng L^{-1} of estrone (E1) induced intersex of male Japanese medaka (*Oryzias latipes*) (Metcalfe et al., 2001). The estrogenicity of EDCs evaluated by a yeast estrogen screen (YES) bioassay is expressed in terms of estradiol equivalent factors (EEFs) (Beek et al., 2006). Higher EEF value corresponds to greater estrogenic potency. As shown in Table 1, the most biologically active estrogen is the synthetic estrogen EE2, which displays 1.25-fold higher potency than E2. Generally, estrogens exhibit up to six orders of magnitude higher estrogenicity in the YES than other major pharmaceuticals and personal care products (PPCPs) (Beek et al., 2006). In the current review, the three natural estrogens E1, E2 and estriol (E3), and a synthetic estrogen (EE2) are considered and the scope is limited to the aquatic ecosystems. The physical and chemical properties together with the structure of the four common estrogens are displayed in Table 1.

Estrogens, naturally produced in living creatures or as medicine administrated to humans and livestock, are excreted, either in free form or as their conjugated counterparts, primarily through urine but also in the feces. These estrogens end up in the aquatic environment through discharges of wastewater treatment plants (WWTPs), animal waste disposal and runoff of field applied hormone-bearing materials (manure, sewage sludge and biosolid, etc.). From a global perspective, concentrations of estrogens in the sewage influents ranged 7.3–197 ng L^{-1} for E1, 4.9–48 ng L^{-1} for E2, and (<0.2)–(<11) ng L^{-1} for EE2, which were eliminated within sewage treatment plant with an average removal rate of 78% (E1), 89% (E2), and 74% (EE2) (reviewed by Xu et al. (2012)). Numerous studies reported the occurrence of estrogens in the aquatic ecosystems worldwide. A recent review by Adeel et al. (2017) summarized in detail the occurrence of estrogens (E1, E2, E3, and EE2) in river and surface waters on a global scale. Generally, the concentrations were extremely variable ranging from below detection limit to hundreds of ng L^{-1}, depending on sampling countries.

Table 1
Physicochemical properties of major estrogens considered in this study.

Estrogens	Molecular weight	Log K_{OW} at pH 7 [a]	Water solubility at 20 °C (mg L^{-1}) [b]	pK_a [c]	EEF [d]	Structure
E1	270.37	3.43	13	10.3	0.25	
E2	272.39	3.94	13	10.6	1	
E3	288.39	2.81	13	10.05	5.9×10^{-3}	
EE2	296.41	4.15	4.8	10.4	1.25	

a,b Ying and Kookana (2005).
c.Yamamoto et al. (2003); Adeel et al. (2017).
d. Estradiol equivalent factor (EEF) (Beek et al., 2006).