Marine Pollution Bulletin 64 (2012) 75–79

Contents lists available at SciVerse ScienceDirect

Marine Pollution Bulletin

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

Occurrence of selected estrogens in mangrove sediments

Sandro Froehner [a,*], Karina Scurupa Machado [a], Elisa Stefan [a], Tobias Bleninger [a], Edson Cordova da Rosa [b], César de Castro Martins [c]

[a] Department of Environmental Engineering, Federal University of Parana, Curitiba – PR 81531-980, Brazil
[b] Senai Cetind, Lauro de Freitas – BA 42000-000, Brazil
[c] Centro de Estudos do Mar, Federal University of Parana, Pontal do Parana – PR 83255-000, Brazil

ARTICLE INFO

Keywords:
Mangroves
Estrogens
Sexual reproduction
Environmental impact
Sewage contamination

ABSTRACT

This paper presents results related to the occurrence and distribution of estrogens along the Brazilian coast. Three mangrove areas were chosen to evaluate the presence of estrogens in surface sediments of mangrove forests. The presence of estrogens was observed in all studied sites. 17-α-Ethinylestradiol (EE2), a synthetic estrogen, was the most common and has been found in higher concentration (0.45–129.78 ng/g) compared to 17-β-estradiol (E1) and estrone (E2) (both being natural estrogens). The concentrations of E1 and E2 ranged from 0.02 to 49.27 ng/g and 0.03 to 39.77 ng/g, respectively. Theoretically, under anaerobic conditions EE2 can be reduced to E1 even in environments such as sediments of mangrove forests, which are essentially anaerobic. Even if the concentrations of estrogens seem to be insignificant in some samples, the effects remain uncertain.

1. Introduction

Estrogens or steroids are compounds involved in sexual reproduction of both, men and women, acting as chemical messengers. The mechanism of estrogens in human organisms is simple: cells identify the hormones through receptors that are specialized by protein structures in molecular recognition (Simmonds, 1992). Estrogens are the predominant female hormones secreted by the gonads and adrenal glands of humans and animals. They stimulate the development and maintenance of the health of the reproductive tissues, breasts, skin, bone maturation and brain (Filby et al., 2007; Giese, 2003; Noppe, 2003). All steroid hormones exert their action by passing through the plasma membrane and binding to intracellular receptors (Ying et al., 2002) and are metabolized in the liver. Estrogens are classified as natural or synthetic. 17-β-Estradiol (E2) is the most important natural female estrogen (Fig. 1) and the base for the development of synthetic estrogens, such as 17-α-ethinylestradiol (EE2), the main compound used in contraceptives.

The endocrine system regulates hormonal processes in the body. Some chemicals appear to be able to mimic estrogens and, therefore, to disrupt homeostasis. The most widely studied estrogen function is that of an estrogen receptor. Several substances are known to mimic natural estrogens, such as polychlorinated biphenyls, alkylphenols, phthalate esters, and also the contraceptive pill component 17-α-ethinylestradiol (Thomas et al., 2004). Even natural estrogens can cause damage when released to the environment (Kirk and Christopher, 2003; Takeshi et al., 2003).

Generally, the origin of estrogens in the environment is poorly or untreated domestic sewage discharged into water bodies (Jobling et al., 1998). According to the literature the estrogens are not completely removed in Wastewater Treatment Plants (WWTP), and usually around 40% are left in secondary treated effluents from conventional WWTPs (Ternes et al., 1999; Froehner et al., 2011). The quantity of excreted steroids depends on sex, race, hormonal status, stage of menstruation, use of contraceptives and pregnancy (Young et al., 2004).

It is known that estrogens may interfere with the normal functioning of endocrine systems, therefore affect reproduction and development in wildlife (Jobling et al., 1998). Effects on human reproduction are also suspected. Assessment of the aquatic toxicity data indicates that concentrations of ng/g can induce feminization of fishes, however main effects on invertebrates and humans still remain uncertain (Sumpter and Johnson, 2005). Toxic estrogens are estrone and 17-β-estradiol, since they are found in different compartments of the environment at levels higher than their Lowest Observable Adverse Effect Level.

Recently, it has been suggested that sex hormones appear to influence the human immune system (Bouman et al., 2005) in addition to effects on sexual differentiation and reproduction. Synthetic steroids used in contraceptives, mainly originate from humans. Another potential source of estrogen contamination are cattle feedlot effluents and agricultural run-off when sewage and manure is used as fertilizer (Lintelmann et al., 2003; Orlando et al., 2004; Soto et al., 2004; Young et al., 2004). Moreover,

* Corresponding author.
E-mail address: froehner@ufpr.br (S. Froehner).

0025-326X/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2011.10.021

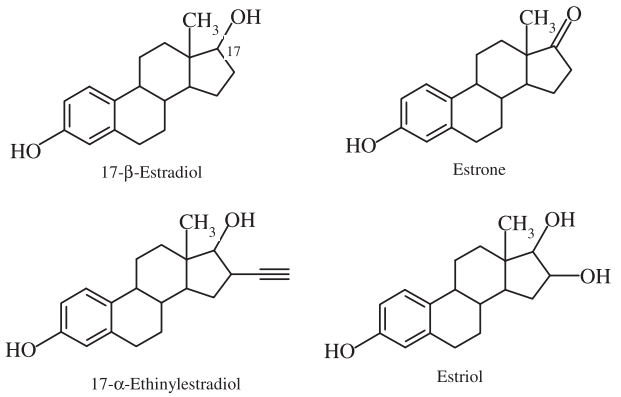

Fig. 1. Chemical structures of most common estrogens found in environment.

estrogens (hormones) are used in supplements of animal husbandry and aquaculture (Kuster et al., 2004; Orlando et al., 2004).

Estrogens are released in the environment as inactive conjugates (mainly glucuronates and sulfates). However, deconjugation by bacterial enzymes in WWTPs or in the aquatic environment, reactivates these conjugates to biologically active parent compounds (Johnson et al., 2000; D'Ascenzo et al., 2003). In the aquatic environment, E2 is rapidly biodegraded to E1 which in turn is degraded to E3 (Juergens et al., 1999). EE2 is designed to resist degradation, thus having it's a low degradation rate. The presence of estrogens in the environment is well documented, for instance, in marine sediments (Isobe et al., 2006; Braga et al., 2005) and in rivers (water and sediments) (Holthaus et al., 2002). However, very few studies documented the occurrence of these compounds in estuarine and marine environments (Baeyens et al., 1998; Thomas et al., 2004).

It has been reported that estrogens are quite common in river waters and sediments. Marine environments are equally susceptible to the presence of such compounds. Although there are few studies showing the presence and fate of estrogens in estuarine environments, even less works involve mangrove forests.

The presence of such compounds, however, could present an elevated risk to organisms in mangroves, which are considered as a more sensitive ecosystem. Mangrove forests are important inter-tidal estuarine wetlands along the coastline of tropical and subtropical regions. Mangrove's unique features such as high primary productivity; abundant detritus, rich organic carbon and anoxic/reduced conditions make them a preferential site for the uptake of anthropogenic pollutants (Tam et al., 2001). Apart from natural contributions, mangroves are also susceptible to inputs of pollutants from diffuse anthropogenic sources. In most coastal areas, mangroves are significant receptors of such pollutants, from the atmosphere, continental surface and river runoff and tidal currents.

A screening for estrogens in mangrove areas was undertaken in three regions along the Brazilian coastline. Mangroves occur along ocean coastlines throughout the tropics, and provide numerous ecosystem services, including fisheries production and nutrient cycling (Donato et al., 2011). Estuarine ecosystems are traditionally known as nursery areas important for the earlier phases of life cycles of both estuarine-resident and temporary resident species. In fact, even the populations that inhabit the coastal regions can use the mangrove and lagoon areas for breeding and spawning activities (Chaves and Bouchereau, 2000).

The Brazilian coastal region holds one of the world's largest mangrove areas of ca. 13,800 km^2, generally dominated by only two species (*Rhizophora mangle* and *Avicennia* germinans), which together constitute more than 80% of the mangroves in Brazil (Behling et al., 2006). The importance of these mangroves is widely recognized in numerous studies (Sovernigo, 2009; Mater et al., 2004; Machado et al., 2002a). With a net production of 350–500 g/cm y mangroves are highly productive, representing the basis of a rich biological system which is an important food supply for local human populations (Behling et al., 2006). In addition, mangroves form protective barriers against wind damage and erosion. Although the ecological importance of mangroves is being recognized, they are still decreasing in areas all around the world, thus giving importance to the evaluation of the presence of such chemical compounds.

1.1. Study areas

The main purpose of this work was to study the presence of estrogens in three Brazilian mangrove areas, one located in the tropical northeastern region, and two located in the sub tropical southern region of Brazil (Fig. 2). These mangrove regions were already studied by other groups before, which indicated contamination by sewage (Mater et al., 2004; Reis-Filho et al., 2010; Santos et al., 2008; Machado et al., 2002b). However, no studies have been undertaken yet to determine the presence of estrogens in the mangrove sediments. As described in the previous studies (Machado et al., 2002a; Mater et al., 2004; Reis-Filho et al., 2010; Santos et al., 2008), the settlements near the studied mangrove areas neither have a sewage collection system nor a wastewater treatment installation. Local sanitation solutions generally apply septic tanks, but the studies reported several illegal discharges. Thus, it has not yet been possible to associate specific discharges or source regions to contaminated sites.

1.1.1. Joanes River Mangrove Area – Salvador (JRM)

The Joanes River Mangrove Area is located in the metropolitan region of Salvador, one the largest cities of Brazil, with more than 3.5 million inhabitants (Reis-Filho et al., 2010). It belongs to the Joanes–Ipitanga preservation area. Unfortunately, there is a historical degradation process due to the proximity of industrial areas near the mangrove area. Furthermore, there are uncontrolled settlements within that area. JRM mangrove's area has approximately 14 km^2.

1.1.2. Itacorubi Mangrove Area – Florianopolis (ITM)

The ITM mangrove is a mixed basin type of mangrove forest, located in the central sector west of the Island of Santa Catarina,

Fig. 2. Map of Brazilian coast showing the location of studied mangroves. JRM – mangrove of Salvador; ITM – mangrove of Itacorubi; GRP – mangrove of Guaratuba.