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Occurrence, source analysis and risk assessment of androgens, glucocorticoids and progestagens in the Hailing Bay region, South China Sea

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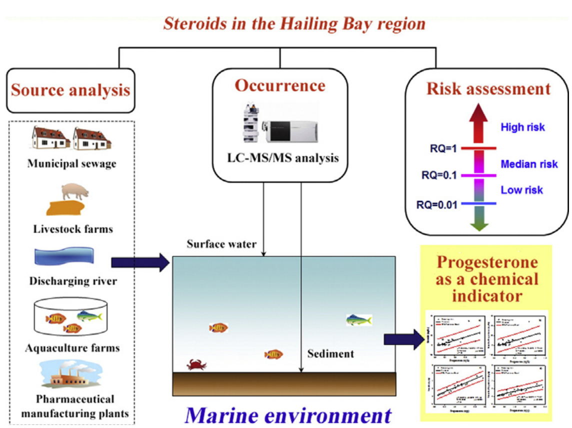
HIGHLIGHTS

- Forty steroids were systematically investigated in marine environment.
- The distribution of steroids was significantly correlated with COD and NH_4-N.
- Untreated municipal sewage is the main source of steroids in the Hailing Bay region.
- Progesterone could be a chemical indicator of steroids.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence and spatial distribution of 40 steroids in the environmental matrices of the Hailing Bay region, South China Sea, were investigated by rapid resolution liquid chromatography–tandem mass spectrometry (RRLC–MS/MS). Seventeen, 14 and 11 of 40 steroids were detected with the concentrations ranging from 0.04 (testosterone) to 40.00 ng/L (prednisolone), 1.33 (4-hydroxy-androst-4-ene-17-dione) to 1855 ng/L (androsta-1,4-diene-3,17-dione) and <0.19 (androsta-1,4-diene-3,17-dione) to 2.37 ng/g (progesterone) in the seawater, the municipal sewage discharged effluent and the sediment samples, respectively. The concentrations and risk quotients (RQs) of the steroids detected in the water samples decreased in the order of municipal sewage discharge site > wharves ~ aquaculture zones ~ tourism areas > offshore areas. The distribution of steroids in the marine environment was significantly correlated with the levels of chemical oxygen demand (COD) and ammonium nitrogen (NH_4-N). Source analysis indicated that untreated municipal sewage was the main source

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of steroids in the marine environment. Furthermore, progesterone was found to be a reliable chemical indicator to surrogate different steroids in both the water and sediment phases based on the correlation analysis.

1. Introduction

Currently, the widespread occurrences of steroids in the environment and their potentially adverse effects have become great concerns among scientific community and the public. Steroids, including natural and synthetic forms, could interfere with fertility and feminization of aquatic organisms at concentrations as low as ~1 ng/L (Fick et al., 2010; Huang et al., 2013; Zeilinger et al., 2009). Wastewater treatment plants (WWTPs), including municipal, livestock, hospital, and pharmaceutical manufacturer WWTPs, are regarded as the most important sources of steroid pollution in the environment. Due to the incomplete removal or direct discharge, steroids have been widely detected in the environment (Bradley et al., 2009; Casey et al., 2004; Chang et al., 2009; Liu et al., 2012a). The reported concentrations of steroids ranged from not detected (ND) to 8150 ng/L in the influents of WWTPs (Chang et al., 2008, 2011; Fan et al., 2011; Liu et al., 2011; Sim et al., 2011), ND to 529 ng/L in the final effluents (Sim et al., 2011), 2.2 to 14400 ng/g in livestock feces (Liu et al., 2012b), 1.6 to 10800 ng/L in livestock wastewater (Liu et al., 2012a, 2012b), and 0.8 to 465 ng/L in receiving surface water (Liu et al., 2012a, 2012b).

Most previous studies on steroids focused on their occurrence in freshwater environments, while few studies in marine environment could be found due to the difficulty in sample collection or determination limitations. In recent years, marine environment has become a major concern due to its value to socioeconomic development and human health, especially its function as the pollutant sink. It was found that terrestrial wastewater was one of important pollution sources to marine steroid pollution (Atkinson et al., 2003). Estrogens have been detected in marine water and sediment with concentrations ranging from ND to 0.76 ng/L (Ronan and McHugh, 2013) and ND to 3.60 ng/g, respectively (Braga et al., 2005; Isobe et al., 2006). In Europe, a list of priority pollutants with endocrine-disrupting properties defined by the Water Framework Directive (WFD, 2000), have been required for the substantial monitoring in transitional and coastal waters. Among which, two estrogens with average concentrations at 0.08 (17β-estradiol) and 0.007 ng/L (17 α-ethinylestradiol) have been proposed to be included in this list. However, other groups of steroids, such as androgens, glucocorticoids, and progestagens have received little attention.

The rapid economic development in China has caused serious pollution problems, which adversely affect water quality in the offshore (CMEB, 2013). The Hailing Bay region, including Hailing Bay and Hailing Island, located in Guangdong province of South China, is a famous aquaculture zone as well as tourist destination. Since there is no WWTP in operation in the Hailing Bay region, most wastewater is directly discharged into the marine environment. As a typical semi-enclosed environment, the Hailing Bay receives various pollutants from terrestrial wastewater via municipal sewage, industrial wastewater, and discharging rivers. In our recent study, the occurrence, bioaccumulation, and human dietary exposure via seafood consumption of 24 steroids were investigated in six typical marine aquaculture farms in Hailing Island. Ten, 9, 10, 15 of 24 steroids were detected at concentrations ranging from <0.1 (testosterone) to 40 ng/L (prednisolone), from 0.1 (4-androstene-3,17-dione) to 2.4 ng/g (progesterone), from 0.3 ng/g (testosterone) to 21.4 ng/g (epi-androsterone) and from <0.1 (testosterone) to 560 ng/g (cortisol) (wet weight) in the water, sediment, feed and biota samples, respectively (Liu et al., 2015). However, the occurrence, source analysis and risk assessment of androgens, glucocorticoids and progestagens in the surrounding marine environment of the Hailing Bay region has not yet been investigated. The objectives of this study were to (1) investigate the occurrence and spatial distribution of 40 steroids including androgens, glucocorticoids and progestagens in the marine environment of the Hailing Bay region, (2) evaluate the sources of pollution and assess the corresponding ecological risk, (3) explore the potential application of progesterone as a chemical indicator for different groups of steroids.

2. Materials and methods

2.1. Chemicals and sample collection

High purity standards of 40 natural and synthetic steroids, including 14 androgens, 5 glucocorticoids, 21 progestagens, and 7 internal standards were purchased from various chemical suppliers (Tables S1 and S2). More information about chemicals and materials used in this study can be found in the Supplementary Information (SI). The Hailing Bay region, including Hailing Bay and Hailing Island, is a subtropical drowned valley bay with an average tidal range (irregular semidiurnal tide) of 1.4–1.6 m (Qiu et al., 2006). It covers an area of 880 km^2, with a population of 721,572 (SYJ, 2014). There are three administrative districts, Gaoxin District, Yangxi County and Hailing Island in the Hailing Bay region. The water salinities range from 4.08‰ to 32.14‰, and average seawater temperatures are 21.6 °C and 30.6 °C in winter and summer, respectively (Qiu et al., 2006). The average depths are 5.8 m and 17.1 m in the inner bay (S1–S6) and the outer bay (S7–S22), respectively (Table S3). In addition, the average precipitations are 155–335 mm and 24–59 mm per month in wet seasons (from April to September) and dry seasons (from October to March), respectively. There is a main discharging river, Fentou River, with an average runoff of 28.3 m^3/s in the study area (MWRY, 2012). The seafood output and mariculture area in the study area are 670,675 t/y and 161 km^2, accounting for 96.5% of the total output of aquatic products and 77.1% of the total aquaculture area, respectively (Table S4). Pond culture, cage culture and oyster pile culture are three primary mariculture practices in this area. Most farms, as extensive cultures (low intensity and low management), are practiced in small scales and at comparatively low development stages. Among various seafood, *Lutjanus russelli*, *Lutjanus erythopterus*, and *Trachinotus ovatus* in fish, *Atrina pectinata* Linnaeus, *Meretrix lusoria*, *Trisidos kiyoni* and *Crassostrea rivularis* Gould in mollusks, *Calappa philargius* in crabs, and *Fenneropenaeus penicillatus* in shrimps, are dominant species in the study area.

Thirty-nine water samples (two replicates) and 24 sediment samples (single sample) were collected from the Hailing Bay region during September 23–29, 2013 in the wet season period (Fig. 1). All samples were collected at the low tide of the sampling days. At that time, the dilution effect is minimal, which could better reflect the actual pollution caused by steroids in the marine environment. Considering the potential pollution sources of steroids and their receiving marine environment, these thirty-nine water samples were further divided into five groups: municipal sewage discharge site (D), wharves (W1–W3), aquaculture zones (A1–A7, H1–H3), tourism areas (H4–H7), and offshore areas (S1–S22). The detailed information on sample collection is summarized in SI. Water samples (approximately 0–50 cm below the surface of water grab samples with two replicates for each sampling point) were collected. Each sample was about 5 L. The sample containers had been sequentially cleaned by methanol, deionized water and Milli-Q water, and were rinsed with water from the particular sampling location before use. About 5% (v/v) of methanol was added to each water sample and the sample pH value was adjusted to 3 using 4 M H_2SO_4 in the field. The top 0–30 cm layer of surface sediments was collected with a stainless steel grab sampler. All samples were transported in coolers back to the laboratory. The collected water samples were then