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Estrogenic compound profiles in an urbanized industry-impacted coastal bay and potential risk assessment by pollution indices and multivariative statistical methods

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ABSTRACT

The occurrence and distribution of target estrogenic compounds in a highly urbanized industry-impacted coastal bay were investigated, and contamination profiles were evaluated by estimating total estradiol equivalents (∑EEQs) and risk quotients (RQs). Phenolic compounds were the most abundant xenoestrogens, but seldom showed contribution to the ∑EEQs. The diethylstilbestrol (DES) and 17α-ethinylestradiol (EE2) were the major contributors followed by 17β-estradiol (E2) in comparison with a slight contribution from estrone (E1) and estriol (E3). Both ∑EEQs and RQs indicated likely adverse effects posed on resident organisms. Further, multivariate statistical method comprehensively revealed pollution status by visualized factor scores and identified multiple "hotspots" of estrogenic sources, demonstrating the presence of complex pollution risk gradients inside and particularly outside of bay area. Overall, this study favors the integrative utilization of pollution indices and factor analysis as powerful tool to scientifically diagnose the pollution characterization of human-derived chemicals for better management decisions in aquatic environments.

1. Introduction

With heavily industrialized and urbanized developments, the extraordinary economic boom and the growing population, increasing amounts of anthropogenic pollutants have been continuously discharged into coastal and estuarine areas, in particular those located within or near to urbanization areas, which has raised global concerns especially for endocrine disrupting chemicals (EDCs) due to their widespread distribution and persistent fate in the environment as well as highly potent and toxicological effects to the endocrine systems of humans and wildlife at trace levels (Xu et al., 2016; Zhang et al., 2014). Among the myriad heterogeneous EDCs, a wide range of natural and synthetic substances with high binding affinity to estrogen receptors are thought to be estrogenic chemicals, where steroid estrogens and phenolic xenoestrogens deserve particular attention as the former possesses the high estrogenic power and potential hazard in municipal effluents and the latter has moderately estrogenic potency but massive usage frequently detected in wastewaters affected by industrial inputs (Gong et al., 2011). Due to their intrinsic hydrophobic properties and specific sediment-water and octanol-water partition coefficients ($\log K_{oc}$ and $\log K_{ow}$), estrogenic compounds tend to adsorb strongly on suspended particles and easily deposited in organic carbon-rich sediments when released into the aquatic environment, implying a preferential incorporation into sediments in subsequent partitioning processes and making sediments act as the important sink or reservoir for various estrogens in aquatic ecosystems (Lei et al., 2009; Gong et al., 2011). In this sense, estrogenic levels in the sediment matrix are constantly determined to deliver important information on various pollution events in coastal environments besides the measurements in surface water, which just gave a "snapshot" of the contamination status due to water turbulence and chemical processes (Casatta et al., 2015). Further, estrogens exhibited different environmental behavior dependent on the complicated nature of the sediments, and thus had different sedimentary concentrations in parallel with various physiochemical parameters such as organic carbon contents and grain size distributions, which affect the estrogenic fate, bioavailability and toxicity to aquatic species (Duong et al., 2009). Consequently, an effective program measuring estrogenic levels in each environmental matrix to obtain corresponding composition profiles as well as the sedimentary properties has been proposed, which is crucial to understand contaminant levels of estrogenic compounds, providing more detailed information to evaluate potential risks for protecting the ecosystem in aquatic environment.

To date, diverse approaches have been developed to directly/indirectly evaluate potential effects of the estrogenic compounds in the

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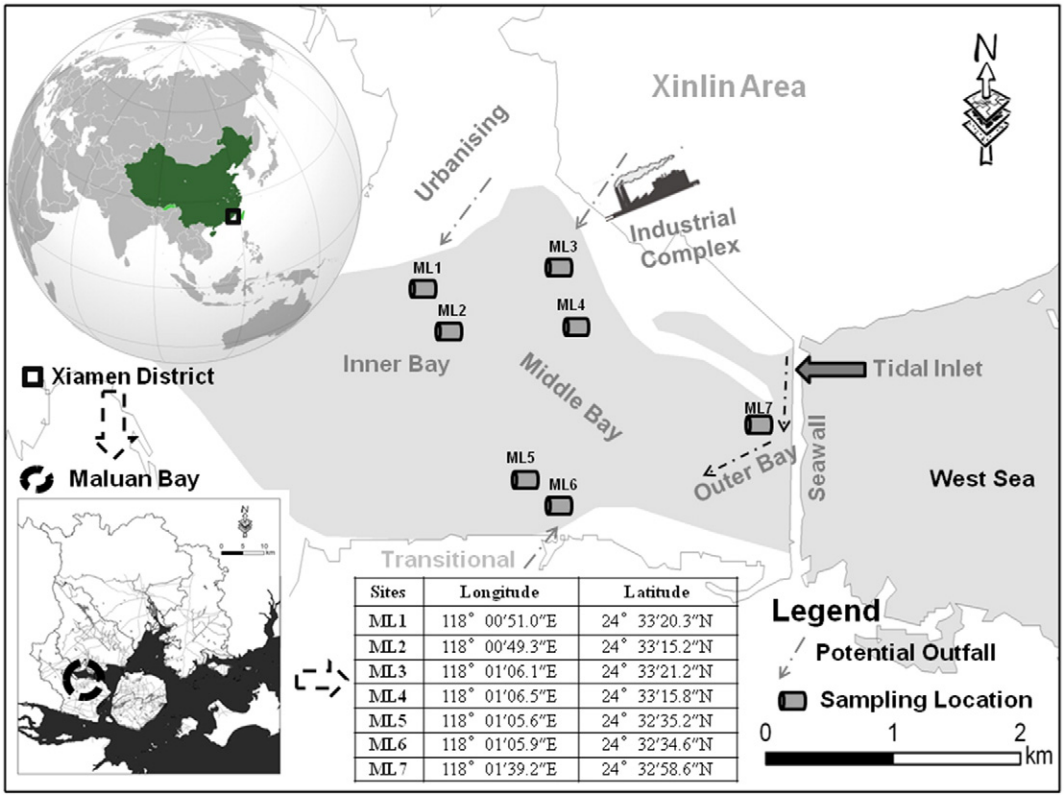
environment. Among the assessment methods, the total estrogenic potential can be quantitatively evaluated in terms of estradiol equivalent concentrations (EEQs) provided that individual concentrations of all active compounds are known, reflecting additive effects of the estrogenic activity for chemical mixtures in samples under real environmental conditions (Pojana et al., 2007). Meanwhile, the risk quotient (RQ), a ratio between the predicted or measured environmental concentrations (PEC or MEC, respectively) and their non-observed effect or predicted no-effect concentrations (NOEC or PNEC, respectively) based on laboratory toxicity data, can describe a general characterization of contaminant risks of individual chemicals, and rank compounds of environmental concern (Xu et al., 2014; Yan et al., 2014). Factually, these calculated pollution indices based on a chemical analysis approach provided useful information about contamination assessment and the preliminary screening of estrogenic compounds in the environment that can be easily communicated to local managers and decision makers for both regulatory and routine monitoring purposes. Nevertheless, the complexity and large variance of datasets in environmental matrixes from coastal areas restricts the utilization of the common index method to comprehensively reveal the real specific state of pollution and identify main contaminant sources with relation to sampling sites (Einax and Soldt, 1999). To overcome this limitation, the application of multivariate statistical methods that can simplify large datasets and further reconstruct more informative variables for making useful generalization to obtain meaningful insights is strongly recommended, which is essential not only to offer more exposition data for comprehensive assessment of the pollution state, but further to rank the range of contaminant influences and screen the pollution in "hotspots" (i.e., study sites strongly affected by anthropogenic inputs) (Wang et al., 2015).

In this study, we focused on Maluan Bay (24°32′47″N, 118°00′38″E), which is a large embayment lagoon along the southeastern coast of China located in the North-West of Xiamen promontory (Fig. 1), and is also a biological productive system with significant ecological functions for fishing and aquaculture. Unfortunately during the past 35 years, the coastal bay is subjected to heavy anthropogenic inputs of contaminants, which received a massive amount of domestic and industrial wastewater and increased great pressure following urban and industrial development as well as marine activities. The main potential sources of estrogenic compounds are: raw domestic sewage from crowded urbanizing places with the limitations of infrastructure, treated municipal effluents and untreated industrial wastewaters from Xinlin industrial complex, together with fish farming wastes through aquacultural runoff and contaminated freshwater from a variety of hospitals directly or indirectly discharged. Geologically, Maluan Bay is subjected to the typical subtropical climate featured with mild temperatures and rich annual rainfalls, facilitating the transport of contaminants to the coastal lagoon through waste discharge, surface runoff and aerial fallout, etc. Moreover, a seawall artificially created in the 1960s limited seawater exchange with the West Sea, which made the contamination of xenoestrogens in closed or semi-enclosed zones receiving effluents worse than those in open sea and further deteriorated its environmental quality seriously. Despite the several expected inputs of estrogenic compounds, to the best of our knowledge, no relevant data are available so far about the occurrence of target chemicals and their potential risk on the coastal wildlife that the general public and scientific community caused great concerns (Zhang et al., 2014). Consequently, the comprehensive assessments related to chemical and ecological risk in Maluan Bay are essentially required.

Specifically, the main objectives of this study were: (1) to investigate the occurrence and spatial distribution of a wide array of estrogenical chemicals by analyzing their concentrations in surface seawater and sediment samples and further associating the estrogenic levels with sediment properties, where for this work selected target compounds including natural estrogens estrone (E1), 17β-estradiol (E2) and estriol (E3), synthetic steroidal estrogens 17α-ethinylestradiol (EE2) and diethylstilbestrol (DES), as well as non-steroidal phenolic xenoestrogens such as 4-nonylphenol (4-NP), 4-tert-octylphenol (4-*t*-OP) and bisphenol A (BPA) were expected to cover most potential estrogens



Sites	Longitude	Latitude
ML1	118° 00′51.0″E	24° 33′20.3″N
ML2	118° 00′49.3″E	24° 33′15.2″N
ML3	118° 01′06.1″E	24° 33′21.2″N
ML4	118° 01′06.5″E	24° 33′15.8″N
ML5	118° 01′05.6″E	24° 32′35.2″N
ML6	118° 01′05.9″E	24° 32′34.6″N
ML7	118° 01′39.2″E	24° 32′58.6″N

Fig. 1. Map of study area and sampling sites in Maluan Bay showing the main geographic features. The co-ordinates are given in the central table. Potential outfalls and waterways or watercourses of tidal seawater from the West Sea are highlighted by arrows.