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Pharmaceutically active compounds and endocrine disrupting chemicals in water, sediments and mollusks in mangrove ecosystems from Singapore

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ABSTRACT

This study investigated the occurrence of bisphenol A (BPA), atrazine and selected pharmaceutically active compounds (PhACs) in mangrove habitats in Singapore in 2012–2013, using multiple tools (sediment sampling, POCIS and filter feeder molluscs). Using POCIS, the same suite of contaminants (atrazine, BPA and eleven PhACs) was detected in mangrove waters in 28-days deployments in both 2012 and 2013. POCIS concentrations ranged from pg/L to μg/L. Caffeine, BPA, carbamazepine, E1, triclosan, sulfamerazine, sulfamethazine, and lincomycin were also detected in mangrove sediments from the low pg/g dw (e.g. carbamazepine) to ng/g dw (e.g. BPA). The detection of caffeine, carbamazepine, BPA, sulfamethoxazole or lincomycin in bivalve tissues also showed that these chemicals are bioavailable in the mangrove habitat. Since there are some indications that some pharmaceutically active substances may be biologically active in the low ppb range in marine species, further assessment should be completed based on ecotoxicological data specific to mangrove species.

1. Introduction

Human pharmaceuticals and various endocrine disrupting chemicals (EDCs), residues of raw and treated wastewaters, have been detected in surface waters, groundwater and soils (Hughes et al., 2013; Tran et al., 2013; Yi et al., 2015). Pharmaceutical residues have also been detected in coastal waters (Bayen et al., 2013; Gaw et al., 2014). In fact, although a substantial fraction of the world's population lives in coastal cities, significantly less attention has been paid to understanding the release of pharmaceuticals in coastal waters and their subsequent impacts on marine ecosystems (Gaw et al., 2014).

Mangrove ecosystems are unique transitional coastal ecosystems generally confined to the tropical and subtropical regions. Mangrove forests are disappearing fast, either because of direct clearance or because they are vulnerable to stressors (e.g. sea-level rise, insect infestation, chemical pollution) (Bayen, 2012; Friess et al., 2011; Giri et al., 2011; Lewis et al., 2011; Lovelock et al., 2015). With regards to chemical pollution, Bayen (2012) noted that very little information is available on the occurrence of compounds other than polycyclic aromatic compounds, conventional persistent organic pollutants (POPs) and trace metals. With regard to contaminants of emerging concern such as pharmaceutical residues, the situation has not evolved much since 2012, and only a few have studied the behavior and the occurrence of these contaminants in mangrove ecosystems. Ramaswamy et al. (2011) had reported the levels of carbamazepine (an anticonvulsant and antiepileptic) and triclosan (an antimicrobial agent) in mangrove waters in India, originating probably from household sewage and industrial effluents. Froehner et al. (2011) detected the presence of estrone (E1), 17-β-estradiol, and 17-α-ethynilestradiol in mangrove sediments in Brazil, which was associated with irregular or illegal discharge of effluents. More recently, Beretta et al. (2014) identified various pharmaceutical and personal care products in one of the largest bays in Brazil, including some mangrove sites.

Pharmaceutically active compounds (PhACs) and herbicides have been reported recently in seawater collected at eight locations around Singapore in June–July 2011 (Bayen et al., 2013). In this earlier study, an apparent increased exposure risk of PhACs and EDCs was observed in the vicinity of Buloh Island, a site adjacent to Singapore's largest protected wetland, Sungei Buloh Wetland Reserve (BUL, Fig. 1). Consequently, the objectives of the present study were to (i) further investigate the presence of PhACs, bisphenol A (BPA) and atrazine in

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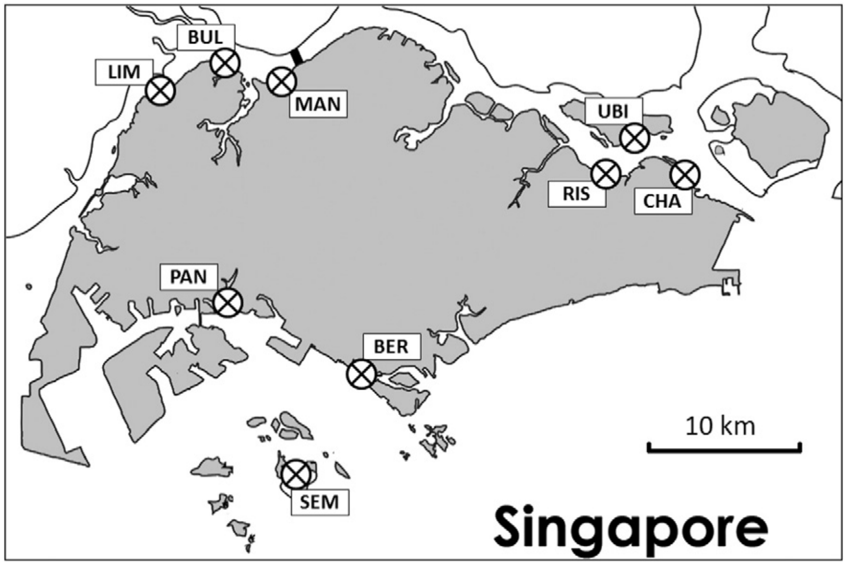

Fig. 1. Mangrove sites of study.

mangrove waters in Singapore, (ii) explore the possibility of burial of these contaminants in mangrove sediments, and (iii) confirm whether they would be bioavailable. Multiple tools were used for this assessment, including sediment sampling, Polar Organic Chemical Integrative Samplers (POCIS) and caged/native mollusks.

POCIS, marketed as AQUASENSE-P by Environmental Sampling Technologies Inc. (St. Joseph, MO, US) have been applied for a range of PhACs and EDCs in temperate zones (Morin et al., 2012). POCIS passive samplers can provide a time-weight average (TWA) concentration, C_{POCIS}, of the contaminants at deployment sites, and make it a tool of choice for risk assessment. POCIS measurements may be influenced by temperature, pH, salinity or agitation (Morin et al., 2012). POCIS were successfully calibrated and deployed in tropical aquatic systems, including dynamic systems such as mangrove waters (Bayen et al., 2014a), explaining their selection for the present study.

Marine bivalve mollusks such as mussels or clams are now well adopted biosentinel species, which have been recently applied for the monitoring of pharmaceuticals in coastal waters (Bayen et al., 2015; Gaw et al., 2014), in combination with POCIS for example (Alvarez et al., 2014; Turja et al., 2015). Two bivalve species were selected in the context of tropical mangroves: the Asian green mussel (*Perna viridis*) and the lokan clam (*Polymesoda expansa*). Green mussels have been successfully used as bioindicators for a range of chemical contaminants in tropical regions in Asia (Bayen et al., 2015; Richardson et al., 2005) and in America (de Astudillo et al., 2002). Lokan clams are widespread in the Southeast Asian mangroves and live buried or half-buried in sediments, and may be used for pollution monitoring in mangroves (Bayen et al., 2005). Green mussels and lokan clams were selected in the present study to explore the bioavailability of PhACs in two habitats of mangroves (rivers and mudflats respectively). The present study was part of a larger project

Table 1
Range and frequency of detection of PhACs and EDCs in mangrove waters in Singapore. ND: not detected; n.a.: not available.

	C_{POCIS} concentration range (ng/L) and frequency of detection in mangrove water ($n = 44$)	Concentration range (ng/g dw) and frequency of detection in mangrove sediments ($n = 72$)	Concentration range (ng/g ww) and frequency of detection in mangrove clam tissues ($n = 36$)	Concentration range (ng/g ww) and frequency of detection[a] in caged mussel tissues ($n = 39$)
Atrazine	<7.0–366 (56%)	n.a.	ND	ND
Bisphenol A	5–1918 (100%)	<0.4–81 (75%)	<0.4–33 (67%)	<0.4–63 (23%)
Carbamazepine	0.06–4.63 (100%)	<0.001–1.3 (64%)	<0.002–0.34 (17%)	<0.003–0.05 (10%)
Caffeine	5–1389 (100%)	<0.1–12 (96%)	<0.06–11 (42%)	<0.1–0.8 (5%)
Chloramphenicol	<0.003–0.70 (14%)	ND	ND	ND
Diclofenac	<0.04–1.7 (9%)	ND	ND	ND
Estrone (E1)	<0.02–2.9 (94%)	ND	ND	ND
Gemfibrozil	<0.77–17.7 (77%)	ND	ND	ND
Lincomycin	<0.04–1.36 (93%)	<0.01–0.04 (8%)	<0.01–0.03 (6%)	<0.015–0.022 (5%)
Risperidone	ND	n.a.	<0.03–0.21 (11%)	ND
Sulfadiazine	<0.04–0.80 (43%)	ND	<0.03–8 (6%)	ND
Sulfamerazine	0.03–0.24 (25%)	<0.01–0.47 (14%)	ND	ND
Sulfamethazine	<0.06–6.26 (80%)	<0.01–0.22 (14%)	ND	ND
Sulfamethoxazole	<0.06–6.26 (80%)	ND	ND	<0.1–3.0 (5%)
Triclosan	n.a.	<0.4–15 (29%)	n.a.	n.a.
Other compounds not detected	Ibuprofen Naproxen Ceftiofur	Ibuprofen Naproxen Furazolidone	Ceftiofur Furazolidone Naproxen Sulfanilamide Tylosin Vancomycin	Ceftiofur Furazolidone Naproxen Sulfanilamide Tylosin Vancomycin

[a] Frequency of detection amongst mussel batches recovered after 28 days in the field.