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Baseline

Pharmaceuticals, personal care products, food additive and pesticides in surface waters from three Australian east coast estuaries (Sydney, Yarra and Brisbane)

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ABSTRACT

The detection rates of pharmaceuticals (Ps), personal care products (PCPs), current-use pesticides (CUPs) and a food additive (FA) in Brisbane River estuary (Queensland), Sydney estuary (New South Wales) and the Yarra River estuary (Melbourne, Victoria) were: Ps: 16/25, 7/25 and 12/25, respectively, CUPs; 28/53, 5/53 and 23/53, respectively, PCPs: 1/3, 0/3 and, 1/3, respectively and FA; 1/1, 1/1 and 1/1, respectively. Diuron was measured in all estuarine samples, simazine, MCPA and 2,4 D were also commonly measured. Pharmaceuticals: carbamazepine, iopromide paracetamol tramadol and venlafaxine were also commonly measured across the estuaries. Generally, analytes were prominent in Brisbane River estuary, followed by Yarra River/Sydney estuary. Inputs of Ps are likely from leakages or effluents of WWTPs; CUPs are potentially from agricultural and parklands via surface run-off in Brisbane River estuary, while for Sydney and Yarra estuaries, which have separate stormwater and sewer systems, sources are likely to be ingression and leakage.

1. Introduction

Some pharmaceuticals (Ps), personal care products (PCPs), current-use pesticides (CUPs) and food additives (FAs) are ubiquitous in the environment, including both estuaries and rivers and have been identified as emerging contaminants. Applications of CUPs (herbicides, insecticides and fungicides) to improve agricultural yield (plants and animals), as well as the use of PPCPs (including antibiotics, hormones, analgesics, blood lipid regulators, cytostatic drugs and antiepileptic) for therapeutic and cosmetic purposes have resulted in contamination of the environment, including water bodies (Radjenović et al., 2008; Liu and Wong, 2013; Kasprzyk-Hordern et al., 2009; Birch et al., 2015; Magnusson et al., 2013; Agrawal et al., 2010; Becker et al., 2009). These compounds may bio-accumulate in non-target aquatic fauna and cause potential adverse effects to aquatic organisms, as well as humans via the food chain (Liu and Wong, 2013; Richardson et al., 2005). While pesticides may be washed into rivers via stormwater drains; or surface runoff (from backyards, farms and parklands), pharmaceutical products, which are often not fully metabolized in the body, culminate in wastewater streams as parent compounds, or metabolites through human and veterinary excretion (Birch et al., 2015; Richardson et al., 2005; Roberts et al., 2016; Ellis, 2006). Similarly, personal care products (insect repellents, UV-filters, anti-microbials, or surfactants (Liu and Wong, 2013)) also enter the sewage stream as these materials are mostly washed down during bathing (Birch et al., 2015), or directly into rivers during recreational swimming. These compounds are also released directly into receiving waters during manufacturing and distribution processes, but usually in negligible amounts (Ellis, 2006). Some breakdown routes, such as biodegradation, photodegradation, or adsorption to particles and subsequent sedimentation may be possible for some of these contaminants (Durán-Álvarez et al., 2015; Yu et al., 2011). Even though waste streams containing these compounds are channelled to wastewater treatment plants (WWTPs), significant amounts are not removed by the treatment processes and are continuously transported into river and estuarine systems via effluent discharges.

Despite the increased contamination of Ps, PCPs and CUPs in fresh and marine water bodies in most parts of the world (Caldas et al., 2013; Meffe and de Bustamante, 2014; Valdés et al., 2014; Bartelt-Hunt et al., 2009; Zhao et al., 2013; Zhang et al., 2012; Zheng et al., 2012; Vidal-

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Dorsch et al., n.d.; Brumovský et al., 2017), investigations of the occurrence and distribution of these contaminants in Australian receiving waters are relatively limited (Birch et al., 2015; Roberts et al., 2016; Ferguson et al., 2013). The few studies carried out, however, showed evidence of the presence of these emerging contaminants in water bodies. For example, in the Sydney estuarine waters, concentration of diuron (a herbicide) was up to 3100 ng/L, while the concentrations of fluoxetine (anti-depressant) and acesulfame (food sweetener) were up to 36 ng/L and 114 ng/L, respectively (Birch et al., 2015).

The waters sampled in the present study receive runoff via stormwater drains, as well as being susceptible to occasional effluent intrusions from sewage/wastewater treatment facilities. Sampling sites were adjacent to varying land-use types, including agriculture, residential, commercial and industrial. Water samples were collected mostly during the dry seasons to minimise dilution effects (Roberts et al., 2016).

The objective of the current investigation is to determine the concentration and distribution of common Ps, PCPs, CUPs and a FA in three important river estuaries servicing the three largest capital cities in Australia. Knowledge from this study is necessary to understand the fate and potential risk of these contaminants to the environment.

The Brisbane River estuary is about 344 km long and drains a catchment of 13,560 km^2 (Liu et al., 2017) and is characterised by varying land-use, including: natural environment, intensive urban use, and agricultural lands (Liu et al., 2017). The river estuary flows from Mount Stanley (salinity < 1 PSU) through the Brisbane City before discharging in the Moreton Bay (salinity > 30 PSU) and sampling points span a distance of 70.5 km (Anim et al., 2017). Detailed information on the sampling sites and a map is provided in an earlier publication (Anim et al., 2017). In addition, sampling locations and salinity of water samples are provided in Fig. 1(A) and Table 1, respectively.

Sydney estuary is 30 km long, up to 3 km wide with an area of 50 km^2. The feature is a drowned-dendritic river valley (Roy and Crawford, 1984), which, under low precipitation, is well-mixed, but is strongly stratified after high rainfall (Hatje et al., 2001; Lee et al., 2011; Lee and Birch, 2012). Typical flushing times are of the order of 5 to 10 days, however, flushing time in the upper reaches of the waterway may be as long as 130 days (Das et al., 2000). The catchment (500 km^2) is highly industrialised and urbanised (86%) (Birch, 1996; Birch et al., 1999) and home to about 4.5 million people (Birch, 2007). Sediments in the estuary are subject to significant contamination by metals (Birch and Taylor, 1999), nutrients (Birch, 1996), polycyclic aromatic hydrocarbons (McCready et al., 2003) and organochlorine compounds (Birch, 1996, 2007) and it is classified as "severely modified" by the National Audit of estuaries (NLWRA) (NLWRA, 2002). In addition to sampling locations (Fig. 1(B)) and salinity information (Table 1), an earlier publication by Birch et al. (2015) provides detailed description of Sydney estuary.

The Yarra River is 175 km long, has a catchment of approximately 5400 km^2 and flows through metropolitan Melbourne with a population of approximately 4 million. The river is subjected to tidal influences for approximately 30 km upstream, while the lower estuary has been extensively modified by commercial activities. The Yarra River is a major sediment contributor to Port Phillip Bay. The estuarine region of the Yarra River extends 22 km upstream from Hobson Bay and may be divided into two sections, i.e. an upper section 1 to 4 m deep and a lower section, which is dredged to depths of 8 to 13 m and includes Port of Melbourne. The Yarra River discharges into Port Phillip Bay, which has a very restricted connection with the ocean. Sampling locations and water salinity are provided in Fig. 1(C) and Table 1, respectively.

Water samples were collected in 500 mL polyethylene bottles at approximately 0.5 m below the water surface using a grab water sampler and the samples were stored on ice before transporting to the laboratory. Sample bottles were rinsed 3 times with site water prior to filling at each site and new pair of nitrile gloves was worn at each sample site. In this work, water samples were collected for the Brisbane River and Yarra River estuaries in December 2017 and October 2017 respectively and compared with previous data for the Sydney estuary where samples were collected in August 2013. Collection of water samples in each case were carried out after long periods of dry weather

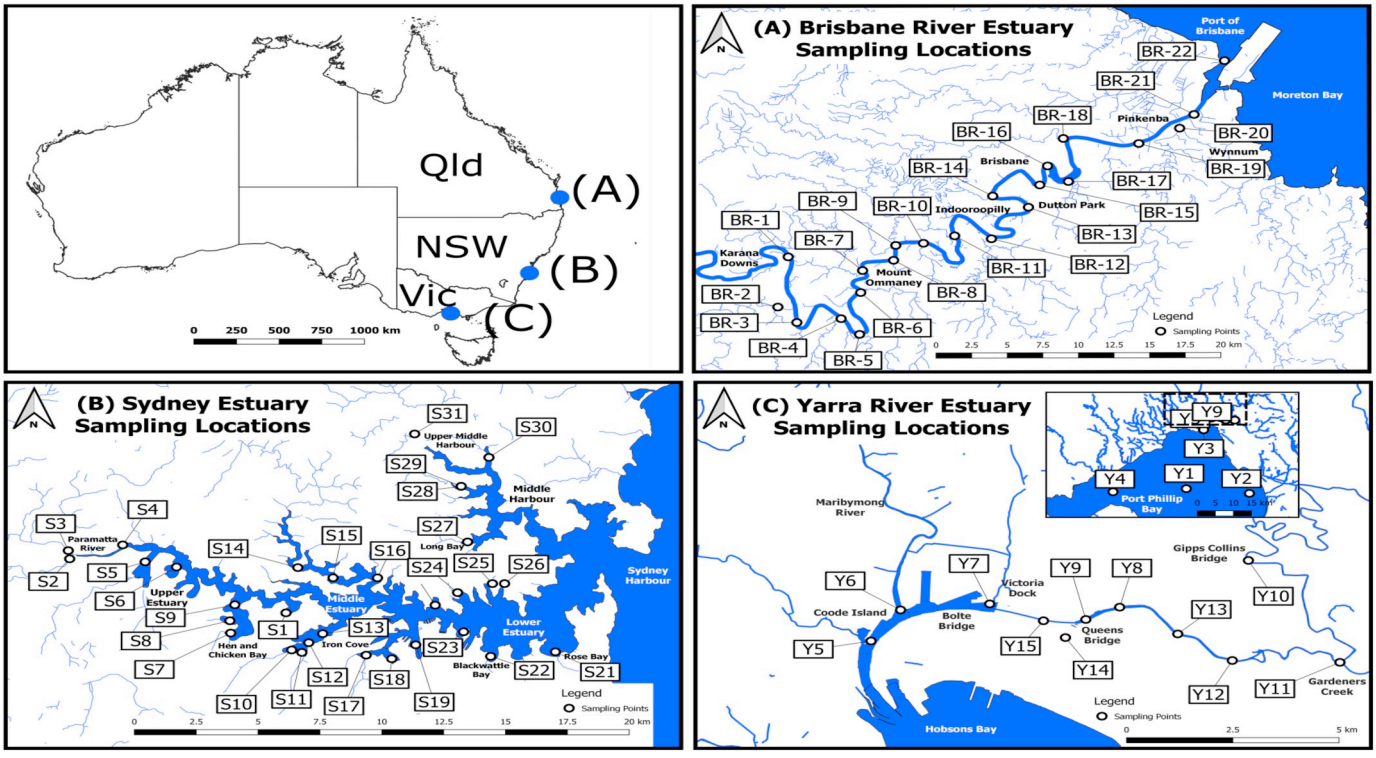

Fig. 1. Map showing the sampling locations; (A) Brisbane River estuary located in Brisbane, (B) Sydney estuary located in Sydney and (C) Yarra River estuary located in Melbourne. Site names are detailed in Table 1.

Table 1
Sampling locations and salinities of the water samples.

Brisbane River estuary			Sydney estuary			Yarra River estuary		
Sample ID	Location	Salinity (PSU)	Sample ID	Location	Salinity (PSU)	Sample ID	Location	Salinity (PSU)
BR-1	Karana downs	0.3	S1	Five Dock	30	Y1	Central Bay	35
BR-2	Bremer river	0.4	S2	Duck River	28	Y2	Carrum	35
BR-3	Mogill	0.5	S3	Parramatta River	28	Y3	Hobsons Bay	35
BR-4	Goodna Creek	0.6	S4	West Ryde Jetty	29	Y4	Longreef	35
BR-5	Woogaroo Creek	0.7	S5	Homebush Bay	30	Y5	Westgate FRW Bridge	35,5
BR-6	Wolston creek	1.1	S6	Brays Bay	30	Y6	Coode Island	17.3
BR-7	Pullen Creek	1.6	S7	Kings Bay (HC Bay)	29	Y7	Bolte Bridge	14.8
BR-8	Mt. Omaney Creek	2	S8	Excile Bay (HC Bay)	30	Y8	Elizabeth Rd Bridge	4.3
BR-9	Jindalee	2.8	S9	Hen and Chicken Bay	30	Y9	Kings Bridge	5.1
BR-10	Centenary Creek	3.8	S10	Iron Cove	32	Y10	Gipps Colins Bridge	0
BR-11	Figtree pocket	6.4	S11	Iron Cove	32	Y11	Gardiners Creek	0
BR-12	Oxley creek	11.4	S12	Iron Cove	31	Y12	Church St Bridge	1.2
BR-13	UQ bridge	15.8	S13	Upper Lanes Cove	30	Y13	Morell bridge	0
BR-14	West end	18.8	S14	Burns Bay (LC)	30	Y14	Yarra Pedestrian Bridge	6.3
BR-15	Goodwill Bridge	24	S15	Central Lane Cove	31	Y15	Webb Bridge	7.2
BR-16	Storey Bridge	25	S16	Lowe Lanes Cove	32			
BR-17	Norman creek	26.6	S17	Rozelle Bay	32			
BR-18	Breakfast creek	28.6	S18	Blackwattle Bay	32			
BR-19	Gateway Bridge	31.2	S19	Darling Harbour	32			
BR-20	Bulimba creek	31.5	S20	Berrys Bay	33			
BR-21	Pinkemba boat ramp	33.1	S21	Rose Bay	34			
BR-22	Port of Brisbane	33.3	S22	Ruchcutters Bay	33			
			S23	Farm Cove	33			
			S24	Neutral Bay	33			
			S25	Mosman Bay	33			
			S26	Quakers Hat	31			
			S27	Long Bay	30			
			S28	Sailors Bay	30			
			S29	Sugar Loaf Bay	30			
			S30	Bantry Bay	28			
			S31	Upper Middle Harbour	29			

with the objective of reducing dilution effects of physico-chemical parameters of the water samples, which were measured in-situ (Table 1). Water samples were frozen at −20 °C and freighted to the National Research Centre for Environmental Toxicology, Brisbane where they remained in storage at −20 °C until extraction. Sample preparation and analysis were carried out for the Yarra and Brisbane River estuaries according to methods used previously for Sydney estuary samples with few modifications (Birch et al., 2015). Defrosted samples were mixed by inversion then poured into 50 mL aliquots, which were spiked with a PPCPs and CUPs stable isotope mix (Fig. SI-1). Samples were then extracted using solid phase extraction (SPE) performed by Queensland Health Forensic and Scientific Services (QHFSS) using established standard operating procedures. Samples were acidified (pH 2) before being passed through 200 mg/3 mL Strata-X SPE cartridges (Phenomenex) preconditioned with methanol and HPLC grade water containing 2% formic acid. After sample loading, cartridges were dried and eluted with 80:20 (v/v) dichloromethane: isopropanol. Samples were dried then reconstituted to 500 µL in 20:80 methanol:Milli-Q water before LC-MS/MS analysis.

Analysis was conducted on an API 6500+ QTRAP Mass Spectrometer (Sciex, Ontario, Canada), equipped with an electrospray (TurboV) interface coupled to a Shimadzu Nexera HPLC system (Shimadzu Corp., Kyoto, Japan). Analytes were separated using a Kinetex Biphenyl column (2.6 µm, 50 × 2.1 mm, Phenomenex) run at 45 °C, and a flow rate of 0.3 mL min^{-1} with a linear gradient starting at 5% B, ramped to 100% B in 5.2 min, then held at 100% for 4.3 min (A = 1% methanol in HPLC grade water, B = 95% methanol in HPLC grade water, both containing 0.1% acetic acid). Equilibration occurred for 3.4 mins at 5% B with flow increased to 0.5 mL min^{-1}. The mass spectrometer was operated in scheduled multiple reaction monitoring mode with positive and negative ionisation switching, using nitrogen as the collision gas.

In the following paragraphs, data obtained from the analysis of Brisbane and Yarra estuarine samples where a total of 82 chemical compounds (Ps, CUPs, PCPs and FAs) were targeted are discussed in comparison with data extracted from a previous study (with some of the same authors in Birch et al., 2015) for the Sydney estuary samples (Birch et al., 2015). Table 2 presents a full list of the analytes and a summary of the concentration ranges across all the three estuaries. A total of 8 Ps (atorvastatin, naproxen, sildenafil, verapamil, hydroxycotinine, ibuprofen, furosemide, caffeine) were below detection limits in any of the samples (Table 2(A)). Fluoxetine was also below detection in the Brisbane and Yarra estuary samples, but measured in the Sydney samples with a detection frequency of 27.2% and a maximum concentration of 36 ng/L. Out of the 25 targeted Ps, up to 16 Ps in at least one sample were measured in the Brisbane River estuary ranging between 4.8% (cotinine and nicotine) and 100% (carbamazepine). Carbamazepine was also measured in 100% of the samples from Yarra River estuary, but only 13.6% for the Sydney estuary samples. The detection and measurement of target CUPs in at least one sample were; 28 out of 53 for the Brisbane River estuary, 5/53 for Sydney estuary (as compared with this study) and 23/53 for the Yarra River estuary (Table 2(B)). Diuron was measured in all samples across the three estuaries with the highest concentration of 96.7 ng/L measured in the Sydney estuary. Also, atrazine, metolachlor and simazine were measured in all samples from both the Brisbane and Yarra River estuaries. While simazine was measured in 54.4% of the Sydney estuary samples, atrazine and metolachlor were not targeted, or reported (Birch et al., 2015). Other CUPs; 2,4 D, MCPA, simazine hydroxyl, imidacloprid, and tebuconazole were dominant in both the Brisbane and Yarra River estuaries with detection frequencies > 80%. Even though three PCPs (DEET, triclosan and salicylic acid) were analysed in this study, the detection of DEET could not be confirmed due to poor chromatograms for the second transitions, whereas salicylic acid contents were below detection limits. Triclosan was measured in both the Brisbane and Yarra River estuaries with detection frequencies of 21.4% and 17.2%,

Table 2
List of target analytes with a summary of detection frequencies (%) and concentration range in the water samples across the three estuaries.

Analyte	Brisbane River estuary		Yarra River estuary		Sydney estuary (Birch et al., 2015)	
	Frequency (%)	Min-Max (ng/L)	Frequency (%)	Min-Max (ng/L)	Frequency (%)	Min-Max (ng/L)
(A) Pharmaceuticals						
Paraxanthine	90.5	< 0.05–10.5	77.4	< 0.05–22	–	–
Atenolol	39.1	< 0.05–7.7	–	< 0.05	–	–
Atorvastatin	–	< 0.1	–	< 0.1	–	–
Carbamazepine	100	1.7–106.4	100	1.7–12.9	13.6	< 0.1–2.7
Citalopram	33.3	< 0.1–2.6	8.6	< 0.1–1.0	–	–
Codeine	35.7	< 0.1–3.0	68.8	< 0.1–3.0	17	< 0.2–9.5
N-Desmethylcitalopram	54.8	< 0.1–5.0	–	< 0.1	–	–
N-Desmethyldiazepam	31	< 0.1–1.9	–	< 0.1	–	–
Fluoxetine	–	< 0.1	–	< 0.1	27.2	< 0.1–36
Gabapentin	95.2	< 0.05–117.6	68	< 0.01–19.8	–	–
Iopromide	83.3	< 0.1–94.3	64.5	< 0.1–13.2	91.8	< 0.2–12.5
Naproxen	–	< 0.1	–	< 0.1	–	–
Paracetamol	57.1	< 0.05–6.0	73.1	< 0.05–29.7	100	5.1–33.9
Temazepam	83.3	< 0.05–37.8	64.5	< 0.05–4.1	–	–
Tramadol	90.5	< 0.1–81.1	77.4	< 0.1–8.9	10.2	< 0.2–5.8
Venlafaxine	85.7	< 0.1–86.2	68.8	< 0.1–10.0	20.4	< 0.1–44.7
Sildenafil	–	< 0.1	–	< 0.1	–	–
Verapamil	–	< 0.1	–	< 0.1	–	–
Hydroxycotinine	–	< 0.1	–	< 0.1	–	–
Ibuprofen	–	< 0.5	–	< 0.5	–	–
Furosemide	–	< 0.1	–	< 0.1	–	–
Caffeine	–	< 0.05	–	< 0.05	–	–
Cotinine	4.8	< 0.1–9.6	8.6	< 0.1–17.4	–	–
Nicotine	4.8	< 0.1–1.6	–	< 0.1	–	–
Hydrochlorthiazide	76	< 0.1–31.7	68.8	< 0.1–9.5	–	–
(B) Pesticides						
Tebuconazole	93	< 0.1–16.6	81.7	< 0.1–2.2	–	–
Fluroxypyr	26.2	< 0.1–21.2			–	–
Pendimethalin	–	< 0.1	–	< 0.1	–	–
Fluazifop	–	< 0.1	–	< 0.1	–	–
Propazine	–	< 0.1	–	< 0.1	–	–
3,4 Dichloroaniline	–	< 0.1	–	< 0.1	–	–
Ametryn	–	< 0.1	–	< 0.1	–	–
Asulam	–	< 0.05	–	< 0.05	–	–
Atrazine	100	1.7–39.0	100	1.7–5.4	–	–
Bromacil	–	< 0.1	–	< 0.1	–	–
Carbofuran	–	< 0.05	–	< 0.05	–	–
Chlorpyriphos	–	< 0.1	–	< 0.1	–	–
Clopyralid	80	< 0.1–19.1	73.1	< 0.1–31	–	–
Desethyl Atrazine	35.7	< 0.05–5.1		< 0.05	–	–
Desisopropyl Atrazine	80	< 0.05–5.5	81.7	< 0.05–13.3	–	–
Diazinon	–	< 0.1	–	< 0.1	–	–
Dichlorvos	–	< 0.1	–	< 0.1	–	–
Diuron	100	1.0–56.8	100	1–38.8	100	15.1–96.7
Fenamiphos	–	< 0.05	–	< 0.05	–	–
Flumeturon	–	< 0.05	–	< 0.05	–	–
Hexazinone	69	< 0.05–10.8	34.4	< 0.05–2.9	–	–
Imazapic	38.1	< 0.1–9.3	–	< 0.1	–	–
Imazethapyr	–	< 0.1	–	< 0.1	–	–
Imidacloprid	90.5	< 0.05–46.1	81.7	< 0.05–7.7	–	–
Malathion	–	< 0.3	–	< 0.3	–	–
Methomyl	9.5	< 0.05–1.43	–	< 0.05	–	–
Metolachlor	100	4.1–128.2	100	1.7–7.8	–	–
Metribuzin	–	< 0.1	–	< 0.1	–	–
Metsulfuron-Methyl	75	< 0.05–12.3	30	< 0.05–8.09	–	–
Picloram	57.1	< 0.1–31.4	43	< 0.1–9.34	–	–
Prometryn	–	< 0.1	4.3	< 0.1–1.3	–	–
Propiconazole	57.1	< 0.1–7.1	21.5	< 0.1–3.4	–	–
Propoxur	–	< 0.1	–	< 0.1	–	–
Simazine	100	1.5–34.2	100	9.1–148.2	54.4	< 0.2–8.0
Tebuthiuron	8	< 0.05–1.1	4.3	< 0.05–1.7	–	–
Terbuthylazine	47.6	< 0.1–32.1	25.8	< 0.1–14.0	–	–
Terbuthylazine-desethyl	–	< 0.1	–	< 0.1	–	–
Terbutryn	–	< 0.1	–	< 0.1	–	–
Simazine hydroxy	97.6	< 0.2–7.6	100	1.4–9.4	–	–
DCPU	2.3	< 0.1–1.5	–	< 0.1	–	–
DCPMU	28.6	< 0.1–2.5	34.4	< 0.1–1.8	–	–
Ametrynhydroxy	90.5	< 0.1–13.6	77.4	< 0.1–2.2	–	–
Metalaxyl	7.1	< 0.1–1.5	–	< 0.1	–	–
Pyrimethanil	–	< 0.1	–	< 0.1	–	–
Mecoprop	–	< 0.1	–	< 0.1	6.8	< 0.2–3.7

(*continued on next page*)

Table 2 (*continued*)

Analyte	Brisbane River estuary		Yarra River estuary		Sydney estuary (Birch et al., 2015)	
	Frequency (%)	Min-Max (ng/L)	Frequency (%)	Min-Max (ng/L)	Frequency (%)	Min-Max (ng/L)
Dicamba	–	< 0.1	–	< 0.1	–	–
2,4,5-T	–	< 0.1	–	< 0.1	–	–
Bromoxynil	–	< 0.1	–	< 0.1	–	–
MCPA	81	< 0.1–68.2	81.7	< 0.1–214.4	74.8	< 0.2–61
2,4 D	97.6	< 0.1–62.7	90.3	< 0.1–8.4	44.2	< 0.2–3.5
Triclopyr	42.8	< 0.2–226.4	4.3	< 0.2–10.5	–	–
Haloxyfop	62	< 0.1–12	51.6	< 0.1–3.7	–	–
Diketonitrile	21.4	< 0.1–1.5	4.3	< 0.1–1.0	–	–
(C) Personal care products (PCPs)						
DEET	–	< 0.05	–	< 0.05	–	–
Triclosan	21.4	< 0.1–2.8	17.2	< 0.1–3.1	–	–
Salicylic acid	–	< 0.1	–	< 0.1	–	–
(D) Food additive						
Acesulfame	78.6	< 0.05–103	100	23.1–70.0	78	< 0.1–114.1

respectively (Table 2(C)), but not detected in Sydney estuary. Acesulfame, the only food additive analysed, was measured across all estuaries. Detection frequencies of acesulfame ranged between 78% and 100% (Table 2(D)).

It is worth nothing that single grab samples from each location were analysed in this study; hence, comparisons of the data should be made cautiously. Nonetheless, the detection and measurement of pharmaceutical compounds in the samples indicates a source of concern since the compounds can be bio-active even at low concentrations, such as ng/L levels. The summary of results (Table 2) shows that target P/PCPs and acesulfame were present at measurable concentrations across the three river estuaries, however, there was high variability both between analytes and among study areas. This could partly be due to marginal difference in sampling periods, particularly for the Sydney estuary which was sampled about four years before the Brisbane and Yarra Rivers. The mean concentrations of Ps that were commonly measured across all estuaries were: 18.6 ± 27.1 ng/L (carbamazepine), 13.6 ± 18.3 ng/L (iopromide), 9.4 ± 8.9 ng/L (paracetamol), 10.7 ± 16.3 ng/L (tramadol) and 11.8 ± 15.8 ng/L (venlafaxine). Although temazepam, gabapentin and paraxanthine were not detected in the Sydney estuary, their concentrations were dominant in the Brisbane and Yarra estuaries with mean concentrations of 10.5 ± 10.6 ng/L (temazepam), 28.6 ± 28.7 ng/L (gabapentin) and 5.7 ± 3.4 ng/L (paraxanthine) across both estuaries. The variability in concentrations of analyte is also due to different levels of analyte input in the estuaries, which could arise from proximity of effluent (leakages), input to the sampling points, or the level of dilution at a particular sampling point. The mean concentrations of pharmaceuticals for both Brisbane and Yarra River estuaries, apart from paracetamol, were always higher when compared to earlier results for Sydney estuary (Birch et al., 2015). Mean concentrations of pharmaceuticals reported in this work across both Brisbane and Yarra River estuary sites were of the following orders of factors: 20 (carbamazepine), 5 (iopromide) and 3 (venlafaxine) higher than the concentrations reported earlier by Birch et al. (2015) for Sydney estuary, although paracetamol was lower by a factor of 2. This notable difference could reflect continuous inputs of contaminants; thus, Brisbane and Yarra River estuaries which were sampled more recently recorded higher analyte concentrations relative to the Sydney estuary data. Acesulfame (a food additive), which was measured across all estuaries, was however, highest at a site in Sydney estuary measuring up to 114 ng/L. In the Brisbane River estuary, the maximum concentration of acesulfame (103 ng/L) is therefore consistent with the maximum concentration of 114 ng/L measured earlier by Birch et al. (2015) for Sydney estuary, while the maximum concentration of acesulfame in the Yarra River estuary was lower (70 ng/L). Triclosan, a personal care product, which is used as anti-bacterial in a wide range of products (toothpaste, soaps, detergents, and surgical cleaning treatment) though not detected in the Sydney estuary, was relatively low in both the Brisbane and Yarra estuaries with the highest concentration of 3.1 ng/L measured in the Yarra River estuary. The low levels of triclosan may be attributed to biodegradation, particularly photolysis in surface waters (Durán-Álvarez et al., 2015).

To obtain a preliminary assessment of contamination across the estuaries, the concentrations of the dominant pharmaceuticals and acesulfame in the three estuaries were compared in Fig. 2. Statistical summary of some pharmaceuticals that were mostly detected and acesulfame across all sampling points is also presented in Table SI-2, with the respective 25th, 50th, 75th and 90th percentiles for each of the three estuaries.

The distribution across the three estuaries indicates that apart from paraxanthine, paracetamol and acesulfame, the concentration of pharmaceuticals in the Brisbane River estuary is consistently the highest. Higher mean concentrations of pharmaceutical products in the Brisbane River estuarine samples were measured, i.e. 46 ± 30.2 ng/L (carbamazepine), 42.2 ± 33.7 ng/L (gabapentin), 28 ± 25 ng/L (iopromide), 26 ± 19.6 ng/L (Tramadol) and 24.3 ± 8.7 ng/L (venlafaxine) indicating that the Brisbane River contributes a greater proportion of the contaminants across all three estuaries. Higher inputs and potentially less dilution may therefore be occurring along the Brisbane River estuary compared to the Yarra River and Sydney estuaries. Also the high variability within sampling sites along the Brisbane River estuary indicates varying routes of contamination.

Pesticides, including the legacy organochlorines and CUPs, are

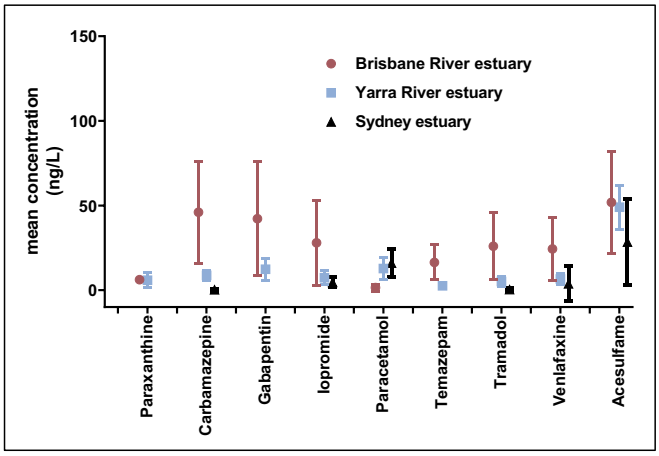

Fig. 2. Comparison of dominant pharmaceuticals and acesulfame concentrations across the studied estuaries.

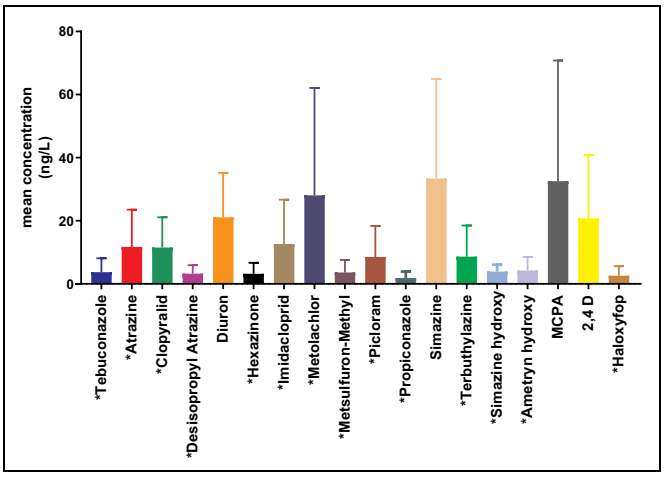

Fig. 3. Mean concentration of pesticides (CUPs) across the three estuaries. Whiskers represent the respective standard deviations. *Represents data obtained for only Brisbane and Yarra River estuaries.

effective against organisms at low concentrations and are expected to localise at the areas of applications (Brumovský et al., 2017). However, the presence of targeted CUPs along the various sampling points in this work suggests their transport beyond the areas of primary applications. It is worth noting that diuron was present at all sampling sites across the three estuaries. Also, atrazine, metolachlor and simazine were measured across all sampling sites for both Brisbane and Yarra River estuaries. This observation suggests continuous inputs of these contaminants into the waterways of the studied estuaries. Despite the lower persistence of CUPs compared to the restricted legacy organochlorine pesticides, the fate of these emerging contaminants needs to be periodically monitored in all three estuaries. The mean concentration of the most commonly measured CUPs across all sampling points is presented in Fig. 3.

The dominant CUPs across all three estuaries were: 23.5 ± 32 ng/L (simazine), 23.1 ± 32.2 ng/L (MCPA), 33.8 ± 23.7 ng/L (diuron), and 14.7 ± 19.7 ng/L (2,4 D) as shown in Fig. 3. Although metalochlor and atrazine were not detected for the Sydney estuary samples, the mean concentrations across both Brisbane and Yarra River estuaries were 31.4 ± 34.7 ng/L (metalochlor) and 13 ± 12.2 ng/L (atrazine). Mean concentrations of tebuconazole, hexazinone, metsulfuron-methyl, simazine hydroxyl and ametryn hydroxyl across both Brisbane and Yarra River estuaries were relatively low, but comparable, ranging between 3.6 and 4.7 ng/L.

Comparison of the distribution of CUPs across the three estuaries is presented in Fig. 4. The concentrations of CUPs show less variability for the Sydney estuary except diuron, and greater variability along the Brisbane River estuary (Fig. 4). This may be due to multiple sources of CUPs contamination along the Brisbane River estuary. Apart from clopyralid, simazine and MCPA, where there was high variability in the Yarra River estuarine samples, the distribution of CUPs were always similar for Sydney estuary and Yarra River estuary with little variability in the mean concentrations. The statistical summaries for CUPs with the nth percentile for each of the estuaries are presented in Table SI-2.

Even though the detection frequency of triclopyr in this work was low for Brisbane River (43%) and Yarra River (4.3%) estuaries, it had the highest maximum concentration (226 ng/L) measured in the Brisbane River estuarine samples. Therefore, triclopyr was included in the discussion to compare the variation across both estuaries (Fig. 4), showing a wide variability across the two estuaries. These results show that apart from simazine and MCPA with mean concentrations of 63 ± 33 ng/L and 60 ± 45.8 ng/L, respectively in the Yarra River, the Brisbane River estuaries was the most contaminated with CUPs (Fig. 4 and Table SI-3). In the Brisbane River estuary, higher mean concentrations were measured for triclopyr (69 ng/L) and metolachlor (50 ng/L) as shown in Fig. 4 and Table SI-3. Other dominant CUPs in the Brisbane River samples were atrazine, diuron, imidacloprid and 2,4 D, which show statistically comparable mean concentrations in the range 21 to 36 ng/L. Pesticides may be transported through stormwater drains, as well as direct surface wash-offs from agricultural lands into the river body. Stormwater drains, as well as animal farms and parklands enter along the Brisbane River and generally, this River estuary has the highest inputs of CUPs contamination, followed by the Yarra River estuary and the least contaminated Sydney estuary. In the Yarra River and Sydney estuaries, stormwater and sewage systems are separated in the catchments. Sewage from Melbourne is discharged from two WWTPs into Port Philip Bay and should not directly impact the Yarra River estuary and in Sydney sewage is discharged via four deepwater outfalls and should also not directly impact the estuary. Possible leakages of sewage into stormwater systems may impact the latter two studied estuaries. Causes of contaminant variability between the three estuaries may also include salinity, tidal flows and flushing time and or differences in sampling periods. For example, salinities across the sampling locations were 0.3–33 PSU for Brisbane River estuary, 0–35 PSU for Yarra River estuary and 28–33 PSU for Sydney estuary. The presence of these emerging contaminants across the three

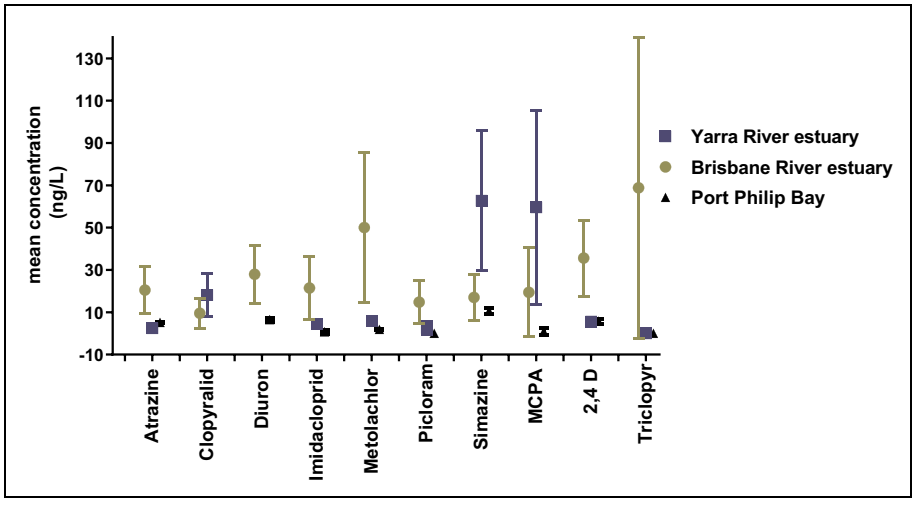

Fig. 4. Comparison of the distribution of CUPs across the three estuaries.

estuaries requires periodic monitoring and fate investigation as these chemicals may potentially impact biota upon exposure.

CRediT authorship contribution statement

Alfred K. Anim:Conceptualization, Investigation, Investigation, Writing - original draft, Writing - review & editing.**Kristie Thompson**:Formal analysis, Writing - review & editing.**Godfred O. Duodu**:Investigation, Writing - review & editing.**Ben Tscharke**:Writing - review & editing.**Gavin Birch**:Conceptualization, Funding acquisition, Writing - review & editing.**Ashantha Goonetilleke**:Writing - review & editing.**Godwin A. Ayoko**:Conceptualization, Resources, Writing - review & editing.**Jochen F. Mueller**:Conceptualization, Resources, Formal analysis, Writing - review & editing.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.111014.

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