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Emerging and persistent organic pollutants in sediment cores from the Singapore Straits: Rising pharmaceuticals, variable caffeine and static PAHs

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ABSTRACT

Five sediment cores of 40 cm length were collected from the Singapore Strait and analysed for emerging and persistent contaminants to assess changing pollutant trends and risk to benthic ecology. Data on the sedimentary accumulation of pharmaceuticals are currently lacking and yet present a potential threat to Singapore's coastal ecosystem. Pharmaceuticals occurred in the order hormones>non-steroidal anti-inflammatory>antibiotics and were highest at the sediment surface then decreased down-core. Similar trends were observed for individual antibiotics, azithromycin 0.18–0.51 ng/g^{-1}, clarithromycin 0.02–0.44 ng/g^{-1} and erythromycin-H_2O 0.01–0.04 ng/g^{-1} as well as anti-inflammatory drug ibuprofen 0.19–8.59 ng/g^{-1}. The non-systematic variation in the hormone estradiol (E2) 3.41–13.83 ng/g^{-1} and drink/food ingredient caffeine 1.27–9.19 ng/g^{-1} was attributed to greater mobility and or post depositional degradation. In contrast, polyaromatic hydrocarbons ($\sum^{16}$PAH) 0.322–32.569 mg/kg^{-1} as well as trace metal mercury (Hg) 0.039–1.022 mg/kg^{-1} were invariant, except for one core which showed a clear-rise and near surface fall tracking TOC% and clay-silt particles. PAH source ratios and parent to alkylated profiles conferred mainly petroleum combustion sources with minor petroleum inputs. Sedimentary PAH and Hg were mostly below established non-statutory sediment quality benchmarks and deemed unlikely to negatively impact benthic ecology. Together PCA and HCA evaluation confirmed similar physico-chemical association for pharmaceuticals and persistent contaminants except for antibiotics. Sediments from Singapore Strait record a recent shift from predominantly hydrocarbon pollution to more complex mixtures spanning pharmaceuticals and caffeine that are suggested but not unequivocally proven to be from on-shore industrial or waste-water discharge sources.

The Republic of Singapore, SE Asia is a successful urban-industrial island city state, 750 km^2, population 5.8 M, GDP $84,734 per capita, located at the tip of the Malaysia Peninsula forming a key hub between maritime routes spanning the Indian and Pacific Oceans (Jackobsen et al., 2022; Sin et al., 2016). Owing to its strategic location at the southern end of the Malaca Straits the Port of Singapore is one of the busiest seaports by tonnage in the world specialising in trans-shipment for approximately 50 % of the worlds crude oil and about 20 % of shipping containers. This maritime-industrial connection serves key coastal electronics manufacturing, oil refining, biotechnology, chemical and pharmaceutical industries that help drive the economy. Consequently, coastal sediments within the Singapore Straits receive chemicals from variety of sources including: 1) treated sewage effluent and road run-off; 2) shipping discharges and portside wastes; 3) crude and refined oil spills; 4) particulates from petrochemical industries (oil refining) and power generation; 5) atmospheric fallout from distant agricultural and forest fire burn events and; 6) ship building and repair (Bayen et al., 2013; Obbard et al., 2007; Sin et al., 2016; Wang et al., 2022).

The occurrence and spatial distribution of pharmaceuticals and endocrine disrupting chemicals have been reported in sea waters from eight locations situated around the island (24 stations) to understand the influence of hydrodynamics, residence times and risk posed to Singapores' coastal marine environment (Bayen et al., 2013). Measurement by LC/MS/MS showed the occurrence of multiple compounds, including gemfibrozil <0.09–19.8 ng/L, triclosan <0.55–10.5 ng/L, carbamazepine <0.28–10.9 ng/L and ibuprofen <2.2–9.1 ng/L. The occurrence of pharmaceuticals in Singapore's sea waters was mainly attributed to

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residence time (tidal flushing) as compared to proximity to water treatment plants (source). Consequently the highest concentrations were observed in sea waters from poorly flushed Buloh Island in the north as compared to hydrodynamically active Changi, E. Jurong Channel and Jurong Island locations (Bayen et al., 2013).

The occurrence and distribution of polycyclic aromatic hydrocarbons (PAH), organochlorine and organo-bromine compounds (PCB & PBDE) in Singapore sediments has been investigated. Evaluation of 22 surface sediments from Singapore's coast reported NE sediments $\sum^{16}$PAH 15.19 to 82.42, mean 48.41 mg/kg^{-1} and SW from 12.65 to 93.85, mean 55.09 mg/kg^{-1} which were classified as moderately contaminated (Obbard et al., 2007). Source identification based on PAH isomeric ratios (phenanthrene/pyrene and pyrene/fluoranthene) and parent PAH distributions confirmed anthropogenic combustion particle sources (Obbard et al., 2007). More recently, PAH and nitro-PAH from atmospheric particulates captured on 2.5 μm filters in south mainland Singapore suggested mainly local traffic emission sources with a possible contribution from Indonesian air masses (haze from burning) during south west monsoon season (Wang et al., 2022).

This study was undertaken to provide a baseline of emerging and persistent contaminants around the southern coast of Singapore using pharmaceutical and PAH exemplar contaminant groups respectively. Short sediment cores (40 cm L) were used to provide an indication of recent change. Supporting TOC, total mercury (Hg) and sediment particle size were taken to contextualise the inventory of organic pollutants. Chemical pollutant data were benchmarked against established consensus sediment quality criteria or where absent relevant ecotoxicological effect studies to provide an indication of risk to benthic ecology.

Sediment cores were collected January 17-20th 2022 using a GOMEX 25 boxcorer deployed from vessel RV Galaxae (SR 3049Z) fitted with stern A-frame and hydraulic winch (Fig. 1). A sub-set of five cores were selected for geochemical evaluation from a total of 20 taken to characterise sediments close to desalination plants; Identifying core codes and locational information are presented in Fig. S1. Sediment cores were continuously sub-sampled at 5 cm intervals (0–40 cm), freeze dried 48 h, sieved to <2 mm and ball milled to <250 μm (Fig. S1) (Vane et al., 2007). Sediment particle size was determined on unground material using a Beckman Coulter LS™ 13,320 MW operated as in Vane et al. (2022a). Quality assurance was achieved using a matrix matched silt dominated reference material (RM-G35D) (Fig. S2). Total mercury (Hg) was analysed using a Milestone Mercury Analyser (DMA-80) instrument (Vane et al., 2019). Quality assurance for Hg was accomplished by analysing high (PACS-2, 3.04 mg/kg^{-1}), and low level (MESS3-1, 0.091 mg/kg^{-1}) certified sediment. Measured values were 3.24 mg/kg^{-1} (RSD 2.41 %, $n = 4$), and 0.66 mg/kg^{-1} (RSD 2.1 %, $n = 2$), 0.10 mg/kg^{-1} (11.25 %, $n = 4$) LOQ 0.005 mg/kg^{-1}.Total organic carbon (TOC), free hydrocarbons (S1) and polymeric (bound) hydrocarbons (S2) were determined by Rock-Eval(6) pyrolysis operated in series; a) pyrolysis 200 °C for 3 min, 200–650 °C at 25 °C/min; b) oxidation stage 200–850 °C at 20 °C/min (Brown et al., 2023; Williams-Clayson et al., 2023). The performance of the instrument was checked every ten samples against the accepted values of the Institut Français du Pétrole standard (Institute Français du Pétrole 160 000, S/N1 5-081840) and instrumental error (standard deviation) TOC ± 0.04 % wt.

Pharmaceuticals were analysed by ultra-high performance liquid chromatography-mass spectrometry (uHPLC-MS) (Vane et al., 2022a; Vane et al., 2022b). Sediments were prepared by spiking with surrogate standards, extracted by ASE, isolated using SPE and spiked with internal standards. Twenty three pharmaceuticals were analysed by uHPLC Acella coupled to a triple-stage quadrupole (TSQ) Quantiva mass spectrometer (LC-MS-MS). Blanks and QC material were run every 10 samples to evaluate instrumental background and instrument performance. Limits of detection LoDof samples were calculated using signal to noise ratio. LoD were defined as the lowest concentration having a S/N > 3 and LoQ were 5xLoD (Fig. S3). PAH were determined by gas chromatography–mass spectrometry (GC–MS). Sediments (1 g) were spiked with deuterated standards, extracted using ASE, isolated using SPE and the eluates spiked with internal standards. Parent and alkylated PAH were measured using a Thermo Scientific Trace 1300-TSQ9000 triple quadropole MS operated in selected ion monitoring (SIM) mode (ionization energy 70 eV) (Vane et al., 2022a; Vane et al., 2022b). The certified reference material (NIST-1944 New York/New Jersey Waterway) and laboratory procedural blanks were interspersed for quality control (Fig. S4).

Singapore Strait sediment particle size distributions are presented in Fig. S5. Cores A8 and MSN2 were comprised of clay (45 %) and silt (45 %) with lower percentage of sand (~5 %) which sit on the boundary between silty clay and clayey silt categories Core sites MSN5 and MSN15 contained greater percentage of sand particles that varied with depth; however, inspection of the down core profiles revealed some differences for example core MSN5 was sand dominated at base (50 %) but fined upward to just 22 % at surface, whereas MSN15 sediment particle size distribution coarsened up-profile becoming more sand dominated

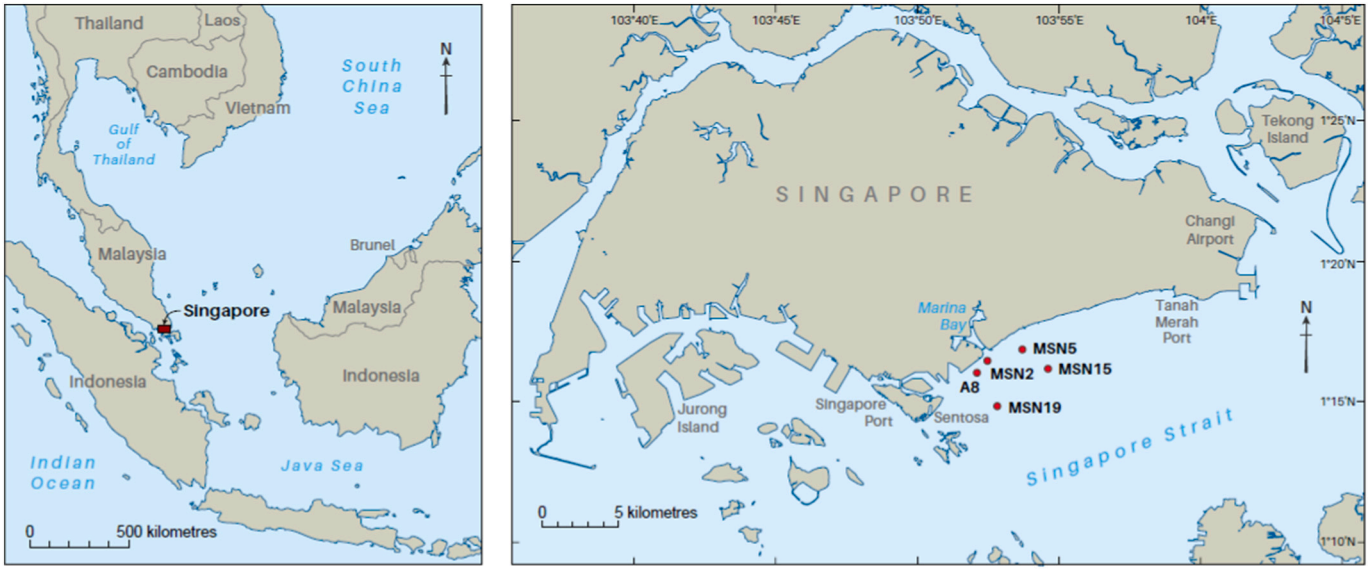

Fig. 1. Site map showing locations of sediment cores from Singapore Strait.

toward surface (Fig. S5). Core MSN19 differed from the others with high sand content (58–74 %), consisting of fine sand (25–38 %) and medium sand (15–30 %) and coarse sand (6–18 %) and correspondingly low clay (6–13 %) and silt (16–18 %). Consequently, sediments from MSN19 were categorised as silty sands or sand (Fig. S5).

The presence of antibiotics in waters and sediment is of worldwide concern as there accumulation contributes to the emergence of bacterial resistant genes which adversely impacts ecological health and ultimately diminishes the effectiveness of key medicines (Thanh Thuy and Nguyen, 2013; Yang et al., 2011; Zhang et al., 2009). In this current study, antibiotic pollution was evaluated using three structurally similar compounds, namely, clarithromycin (FOD 53 %), erythromycin-H_2O (FOD 21 %), azithromycin (FOD 16 %). Clarithromycin was detected in cores MSN2, M5 and A8 with higher values at surface than at lower depths 0.08 to 0.44, mean 0.11 and median 0.04 ng/g^{-1} (Fig. 2). MSN-2 also contained azithromycin 0.18 to 0.51 ng/g^{-1} and erythromycin-H_2O 0.01 to 0.04 ng/g^{-1} which increased toward surface, further supporting the notion that antibiotic sedimentary pollution is increasing in parallel with use and that this is likely to further increase alongside consumption projections (Vane et al., 2022b). However, whilst these trends are clear, it should also be borne in mind that no antibiotics were detected (<LOD) in cores MNSN-15 and 19 which suggests considerable short-scale spatial variation and contrasts with more hydrophobic PAHs. The absence of marine sediment quality guidelines for antibiotics erythromycin, azithromycin and clarithromycin limits discussion on possible ecological effect as the threshold boundaries and accompanying % incidence are at present unknown.

Ibuprofen, the widely used non-steroidal anti-inflammatory ranged from 0.19 to 8.59, mean 2.87, median 2.16 ng/g^{-1} with an FOD of 63 % (Fig. 2). In contrast, acetaminophen (paracetamol) was not observed in any of the sediments (<LOD). Down-core ibuprofen concentrations varied with depth in a non-systematic manner with maxima at 5 cm MSN-2 and M5, 25 cm MSN-15, 15 cm A8 and 22 cm MSN-19 (Fig. 2). Conversely the other non-steroidal anti-inflammatory diclofenac, was only observed at 5 cm in core MSN-2 at a very low concentration of 0.06 ng/g^{-1}. Experimental water-sediment partitioning studies using ibuprofen labelled with ^{14}C report a relatively low affinity for sorption onto sediment (log K_{OW}3.5, D_{OW} 5) with just 9–17 % sorption to sediment and high degradability in sea water/sediment systems (DT90 <6 d) (Löffler et al., 2005). Therefore, the presence of ibuprofen possibly indicates either high input (discharge volumes) and or continuous supply or some other factor not accounted for by physico-chemical properties alone. On an international basis the ibuprofen concentrations are lower than those reported in sewage impacted surface sediments of Santos Bay, SE Brazil 49.0 ng/g^{-1} and Todos os Santos Bay, NE Brazil 14.3 ng/g^{-1}(Beretta et al., 2014; Pusceddu et al., 2018). The general rise in ibuprofen supply and environmental accumulation has been demonstrated from 1970s-2018 in a series sediment cores from Thames estuary, London, UK with values ranging from 3.30 to 12.99, mean 7.66 ng/g^{-1} (Vane et al., 2022b). The toxicological effect of ibuprofen on marine biota has been studied using variety of methods and endpoint criteria. Investigation of the adverse effects of ibuprofen on the benthic worm (Polycheates, *Hediste diversicolor*) using a battery of biomarkers summarised within the integrated biomarker response index reported clear negative impacts at 50 and 500 ng/g^{-1}, whereas, negative impact was not demonstrated at 0.05, 0.5 or 5 ng/g^{-1} (Maranho et al., 2015). Similarly, evaluation of ibuprofen on sea urchin (*Lytechus variegatus*) and bivalve (*Perna perna*) using chronic bioassays for embryo-larval development showed negative effects on both organisms at 15 ng/g^{-1} whereas adverse effect on lyosomal membrane stability in the estuarine bivalve (*Mytella charruanna*) occurred at far lower concentrations 0.15 ng/g^{-1} (Pusceddu et al., 2018). Therefore, taken together these ecotoxicological studies indicate that the ibuprofen concentrations in Singapore Strait sediments are at the lower end of the reported continuum of adverse ecological effects (0.15 -> 50 ng/g^{-1}). The antiepileptic/convulsant drug carbamazepine and betablocker propranolol

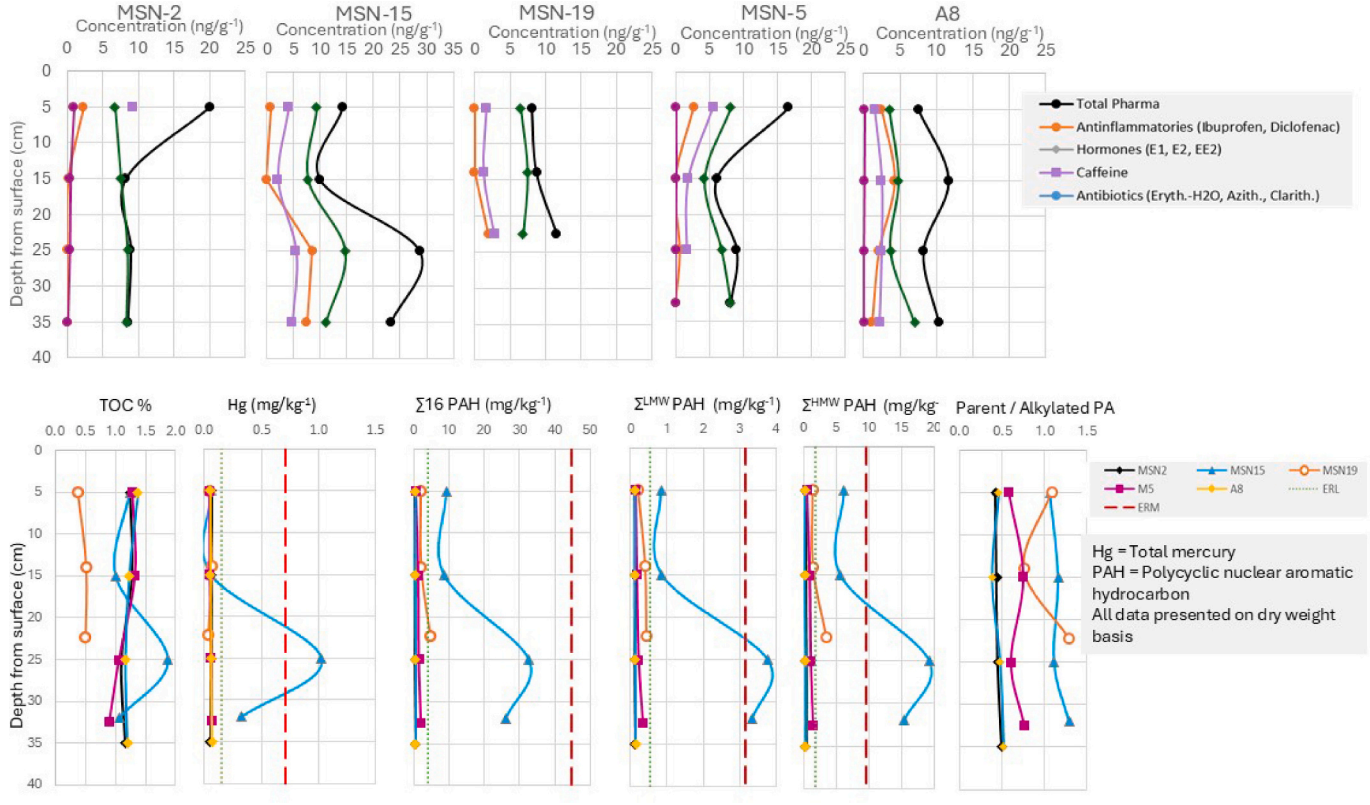

Fig. 2. Down-core variations in sedimentary pollution, Singapore Strait; a) pharmaceutical groups (hormones, caffeine, anti-inflammatory and antibiotics): b) polyaromatic hydrocarbons (PAH). PAH biological effect criteria, effect range low (<ERM no effect); effect range median (>ERM possible effect) (Long et al., 1995).

were only observed at the sediment surface of MSD-2 at 0.15 and 0.78 ng/g^{-1} respectively. This former result is somewhat unexpected given that Carbamazepine is usually one of the most frequently detected pharmaceuticals in estuarine, coastal sediments. Other pharmaceutical compounds, namely, Ifosfamide and cyclophosphamide (cancer treatment) as well as sertraline and norsertraline (anti-depresants) were not detected in any of the Singapore strait sediments (<LOD) which suggests that they are unlikely to impact sensitive sediment dwelling marine ecology.

Anthropogenic release of estrogens, namely estrone (E1) 17β estradiol (E2), estriol (E3) and the xeno-estrogen 17α-ethyinylestradiol (EE2) into the coastal environment mainly occurs from discharge of sewage effluent from waste-water treatment plants or from agricultural run-off containing livestock slurry/biosolids leachate/poultry excreta into river-estuaries (Langston et al., 2005). In this current study, estradiol (E2) was detected in every sediment (100 % FOD) ranging from 3.41 to 13.83, mean 7.17 and median 6.96 ng/g^{-1}, whereas estrone (E1) was observed at lower concentrations (84 % FOD) ranging from 0.11 to 0.68, mean 0.31 and median 0.26 ng/g^{-1} (Fig. 2). In contrast, analytical issues driven by the presence of an interfering (co-eluting compound) prevented reliable reporting of 17α-ethyinylestradiol (EE2). Estriol (E3) and progesterone were not measurable (<LOD).

Previous evaluation of estradiol (E2) accumulating in estuarine and marine sediments has given a range of concentrations depending on proximity to: 1) STW; 2) industrial portside activity and; 3) position downstream of intensive agricultural activity. For example, sewage effluent impacted sediments of the Thames estuary, London, UK ranged from 4.20 to 17.47, mean 10.80 ng/g^{-1} whereas livestock waste receiving Manko tidal flat, Okinawa Island, Japan contained 2 to 23.2 ng/g^{-1} (Tashiro et al., 2003; Vane et al., 2022b). In contrast, lower estradiol (E2) concentrations of 0.07 to 0.59 ng/g^{-1} are reported for Tokyo Bay as compared to Dutch Coast, Ports of Rotterdam and Amsterdam, 4.5–38.4 ng/g^{-1} (Isobe et al., 2006; Legler et al., 2002). Higher values have been reported in sediments from the Mahakam Delta, Indonesia where estrone (E1) 5.21–52.29 ng/g^{-1} and estradiol (E2) 1.22 to 25.12 ng/g^{-1} (Hadibarata et al., 2020). Therefore, based on these comparisons the estradiol (E2) concentrations presented for Singapore strait are similar to other coasts impacted by urban industrial wastes. Given that there are no marine sediment guideline values for hormones it is not possible to infer possible harm to local sediment dwelling marine ecology. However, it is important to consider that the activity (potency) of estradiol (E2) is 5 to 1000 times greater than estrone (E1) and that the former was detected in appreciable concentrations in all sediments and that effects levels for estradiol (E2) in sensitive species are reported to range from just 0.1 to 10 ng/L (Purdom et al., 1994).

Caffeine was detected in 79 % of sediments, varying from 1.27 to 9.19, mean 3.27 and median of 2.46 ng/g^{-1}(Fig. 2). Inspection of the down-core profile revealed a non-systematic depth relationship. For example, core MSN2 and M5 contained the highest caffeine concentrations 9.19 and 5.49 ng/g^{-1} at surface but this then fell below LOQ from 5 cm and 35 cm depth respectively (Fig. 3). Conversely, cores MSN-15, MSN-19 and A8 displayed maximal caffeine values of 5.46, 2.49 and 2.79 ng/g^{-1} at deeper 25 cm depth (Fig. 2). The presence of caffeine in Singapore sediments maybe from treated STW effluent as published data from Jamaica Bay, New York USA and 16 STW in UK confirmed caffeine removal 64–99 % (Benotti and Brownawell, 2007; Gardner et al., 2013). Overall, the presence of caffeine in Singapore sediments tracks increasing use/disposal of coffee, tea, soft drinks and medicines. Laboratory studies have previously reported that caffeine negatively effects the central nervous systems of key marine biota (algae-growth inhibition; bivalvia-oxidative stress; polychaeta-mortality and or oxidative stress; echinoid-reproduction); therefore when taken together the implications are that sediment dwelling organisms in the Singapore Strait could possibly be effected but this hypothesis cannot be proven here (Vieira et al., 2022).

Total mercury (Hg) concentrations were low ranging from 0.039 to 1.022, mean 0.120 and median 0.059 mg/kg^{-1}, with the highest value of 1.022 in core MSN15 at 25 (Fig. 2). From a biological-effect based sediment quality standpoint only the MSN15 25 cm interval exceeded effects range median (ERM) suggesting likely negative health effects on sensitive sediment biota (Long et al., 1995). Sediments from MSN15 32 cm fell between ERL-ERM indicating uncertain effect, whereas all other sediment cores (MSN2, MSN19, M5 and A8) were below ERL, no effect

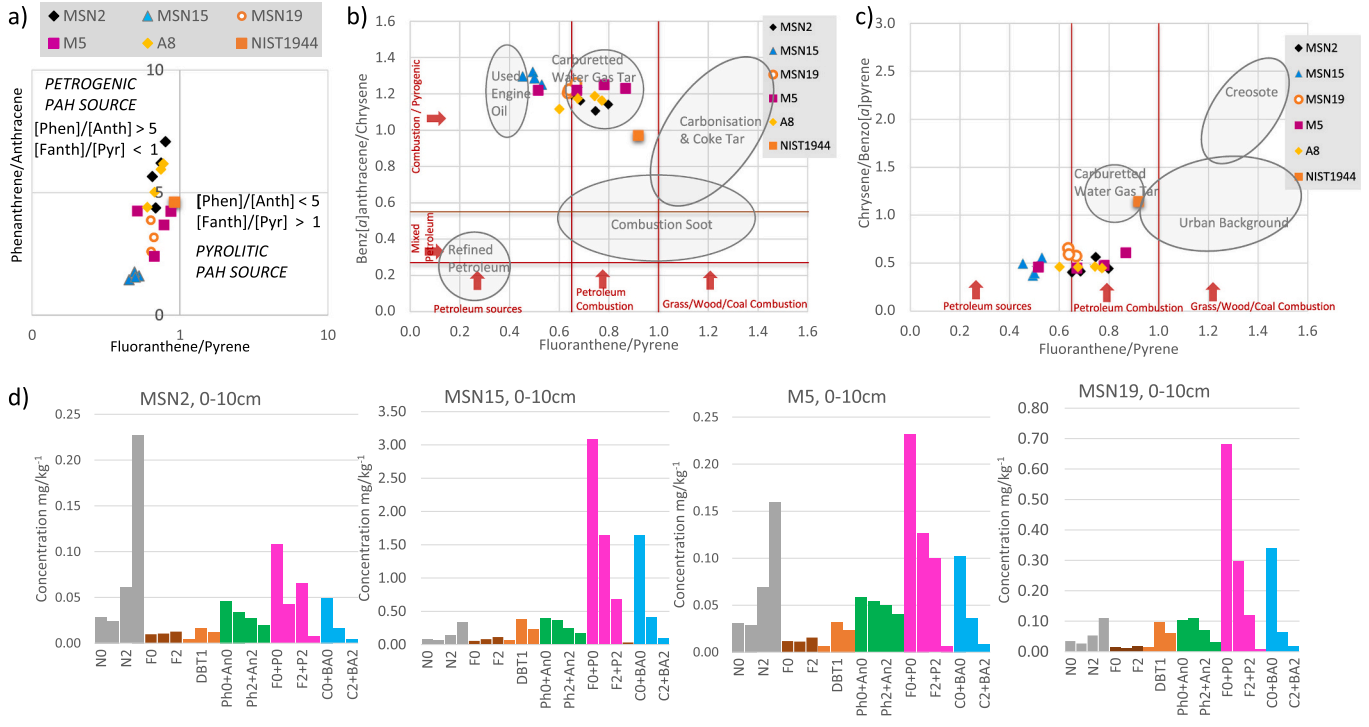

Fig. 3. Polyaromatic hydrocarbon (PAH) source apportionment bi-plots for Singapore Strait sediments.

(Fig. 2). Sediments with higher Hg concentrations were associated finer particle sizes spanning silty clay and clayey silt categories whereas lower Hg were associated with sand dominated material such as that in MSN19 (Fig. 2).

Polycyclic aromatic hydrocarbons (PAH) were detected at all depth intervals (FOD 100 %) ranging from 0.322 to 32.569 mg/kg^{-1}, mean 4.996 and median 1.436 mg/kg^{-1} (Fig. 2). The $\sum^{16}$PAH for MSN2, A8, were low whereas as slightly higher but still moderate PAH values were observed in cores MSN19 and M5. In contrast, core MSN15 had higher $\sum^{16}$PAH ranging from 8.625 to 32.569 mg/kg^{-1}, mean 19.121, median 17.645 mg/kg^{-1} with maximum concentrations at 25 cm depth from surface (Fig. 2). The PAH concentrations presented here for south Singapore are similar to those reported in surface sediments from by Obbard et al., 2007 who evaluated sediments from SW and NE Singapore coast (Fig. 1). On an international basis the mean concentrations and ranges of PAH for Singapore Strait sediments rank above those of Ho Chan and Ma Wan (Hong Kong) Brunei Bay (Brunei), Jakarta Bay (Indonesia), Klang Strait (Malaysia) and oil spill impacted Dalian Bay (China) (Table 1). Similarly, the Singapore strait sediment PAH values were higher than surveys of Cirebon coast (Indonesia), Gulf of Thailand and Phang Nga coast (Thailand), South China Sea (Vietnam), South China (mangrove) coastal sediments (China) and Banyuasin estuary (Sumatra) (Table 1). The most plausible explanation for the higher total PAH values in Singapore Strait being; 1) close proximity to industrialised Singapore mainland; 2) high density of shipping at anchorage and related portside activities and;3) incorporation of atmospheric PAH (haze) due to anthropogenic burning coal and or slash and burn agriculture or to a lesser extent wildfires in adjacent SE Asia countries (Wang et al., 2022).

From an individual PAH standpoint Singapore sediments were dominated by pyrene> fluoranthene>benzo [a] pyrene >benzo [a] anthracene >benzo [b] fluoranthene > chrysene >benzo [e] pyrene benzo [*g, h, i*] perylene (Fig. S6). Comparison of the low molecular weight PAH parent to high molecular weight PAH revealed a greater predominance of high molecular weight PAH parent relative to low molecular weight PAH in all of the sediments (Fig. 3). However, the extent to which this bias summarised by the ratio $\sum^{HMW}/\sum^{LMW}$ occurred varied spatially with low ratios from MSN2 1.3 to 1.7, A8 1.4–1.7 and intermediate ratios from M5 3.1–4.7 and higher ratios from MSN15 4.6–7.3 and MSN19 3.4 to 7.8. Application of Fl/Py to Ph/An PAH source bi-plot was inconclusive in that none of the sediments presented ratios that conferred a definitive petrogenic (upper left quadrant of the bi-plot) or pyrolytic ascription (lower left quadrant of the bi-plot) due in-part to similar fluoranthene and pyrene concentrations driving ratios of 0.6–0.9 (Fig. 3a). Nevertheless, MSN15 sediments PAH clustered in different region of the biplot, suggesting a different PAH source as compared to the other core sites. Inspection of the BaA/Chy and Chy/B [a] P to Fl/Py bi-plots confirmed a combination of petroleum combustion and petroleum PAH sources which broadly align with receipt of wastes from shipping at anchorage and or local onshore power stations such as oil fired Senoko, Tuas and the now decommissioned Pulau Seraya PWST situated on Jurong Island. On the other hand, none of the cores yielded BaA/Chy and Chy/B [a] P to Fl/Py ratios that might suggest significant accumulation of PAH from wildfire or slash and burn agriculture particulate PAH sources carried on air masses from Indonesia during the pre-southwest monsoon season (Fig. 3b, c) (Wang et al., 2022). Inspection of the parent to alkyl substituted PAH (e.g. C0-C3) revealed mainly sloped distributions that decreased with increasing alkylation confirming that the PAH were of mainly pyrolytic origin (Fig. 3d). Inspection of the parent to alkyl PAH distributions down-profile indicated a continuous accumulation of pyrolytic PAH (Fig. S7).

Comparison of Singapore Strait sediment PAH values to established (non-statutory) consensus based marine sediment quality criteria showed that MSN2, M5, A8 and the upper two intervals MSN19 were below ERL criteria for $\sum^{16}$PAH, $\sum^{LMW}$PAH, $\sum^{HMW}$PAH and individual PAH confirming the PAH concentrations were unlikely to harm even sensitive sediment dwelling biota (Fig. 2) (Long et al., 1995). In contrast, all sediments from MSN15 and one from MSN19 exceeded the $\sum$PAH effect range low criteria (ERL) but were below (ERM) suggesting possible, but not definite harmful effects to sensitive sediment dwelling biota (Fig. 3). Benchmarking against $\sum^{LMW}$PAH (100 % incidence), $\sum^{HMW}$PAH (85 % incidence) and benzo [*a*] pyrene (80 % incidence) criteria gave the same no harm effect implication for MSN2, M5, A8 as compared to possible effect for MSN19 (Fig. 2). In contrast, the lowermost intervals of MSN15 exceeded ERM for $\sum^{LMW}$PAH, $\sum^{HMW}$PAH and benzo [*a*] pyrene yielded values that suggest likely harmful effect on local sediment dwelling biota (Fig. 2). Therefore, the PAH SQG evaluation confirmed that only the lower two intervals of MSN15 at 25 and 32 cm depth from surface were likely to adversely impact benthic ecology. Taken together PAH profiles and SQG suggest that the PAH input has remained fairly stable (assuming coastal sediment record is a reliable recorder and not withstanding modifying sorption effect of TOC and surface area of fine sediment particles) and does not pose a significant risk to biota or humans.

Principal component analysis (PCA) was carried out in R on the standardised (centred and scaled) dataset to reduce the dimensionality. Principle component one (PC1) accounts for 52.3 % of the variance within the dataset and refers primarily to the mercury, PAH and

Table 1
Literature based inventory of polycyclic aromatic hydrocarbons (PAH) in coastal and open marine sediments of SE Asia. References within table presented in supplementary data.

Country	Location/land use	Sites	Range mg/kg^{-1}	Mean (Median) mg/kg^{-1}	Reference
Singapore	Singapore Strait	5 cores	0.322–32.569	4.996 (1.436)	This study
Malaysia	Klang Strait, urban port		0.1003–3.447	0.994	(Tavakoly Sany et al., 2014)
Malay	Peninsula, Rural Sea	10	0.02–1.841	0.363	(Retnam et al., 2013)
Thailand	Thai coast	14	0.006–0.228	0.05	(Boonyatumanond et al., 2006)
Thailand	South China Sea	15	0.00259–0.155	0.0183	(Pang et al., 2022)
Thailand	Phang Nga Coast	77	0.0126–0.272	0.0645	(Tipmanee et al., 2012)
Thailand	Gulf of Thailand	92	0.0026–0.0781	0.0194	(Hu et al., 2017)
Brunei	Brunei Bay	14	0.826–2.955	1.495	(Sharifi et al., 2022)
Indonesia	Jakarta Bay, Urban industrial	8	0.187–0.916	0.437	(Aziz et al., 2021)
Indonesia	Jakarta Bay	22	0.03–2.6	0.396	(Dwiyitno et al., 2016)
Indonesia	Cirebon Coast	27	0.000002–0.0422	0.00553	(Khozanah et al., 2019)
Vietnam	South China Sea	16	0.0247–0.275	0.146	(Yang, 2000)
Vietnam	South Central Coast	5	0.038–0.20	0.071	(Nguyen et al., 2024)
Vietnam	Can Gio, mangrove coast	18	0.00073–0.518	0.062 (0.0086)	(Thuy et al., 2021)
Hong Kong	Ho Chung		1.162–3.322	2.022	(Yu et al., 2005)
Hong Kong	Ma Wan		0.791–3.751	2.063	(Tam et al., 2002)
China	South China, mangrove coast	9	0.024–0.238	0.082 (0.061)	(Vane et al., 2009)
Sumatra	Banyuasin estuary	5	0.00316–0.023	Not given	(Putri et al., 2020)
China	Dalian coast (oil spill)	20	0.073–1.90	0.51	(Liu et al., 2013)

pharmaceutical content of the sediment, except for antibiotics (Fig. 4). Principle component two (PC2) explains a further 29.2 % of the variance and primarily refers to the grain size and the antibiotic content of the sediments. As expected, sand % and silt/clay % are strongly negatively correlated. PAHs, pharmaceuticals (excluding antibiotics), mercury and S1 are closely correlated, as are TOC and S2. Antibiotics appear to have no correlation with any other organic or trace metal component but appear to be closely correlated with grain size. Cores MSN-2 and A8 are categorised as silt/clay rich sediments with high quantities of antibiotics and low PAH, mercury, hormone and anti-inflammatory content. Similarly, MSN-5 has low organic content, although some samples have appreciable quantities of antibiotics, and a range of grain sizes. MSN-19 is categorised as sands with very low organic content and core MSN-15 represents sandy sediments with variable quantities of PAHs, mercury and pharmaceuticals (excluding antibiotics).

Hierarchical cluster analysis (HCA) was conducted on the standardised (centred and scaled) dataset in R, with clusters determined using Ward clustering and Euclidian distance matrix (Fig. 4). Cluster stability was approximated using an unbiased bootstrap resampling (n = 10,000). Interpreted hierarchical clusters are consistent with the PCA results, demonstrating a clear control of organic content (PC1) and grain size (PC2) on site clusters. Cluster A, which includes samples from MSN-15 (20–30 cm and 30–34 cm depths), represents clays/silts which are organic rich (excluding antibiotics). Clusters B and C, including all samples from MSN-2, A8 and some M5, are organic poor silts/clays, although B (MSN-2, 0–10 cm depth) has an appreciable quantity of antibiotics. Clusters D (samples from core MSN-19) and E (containing both M5 and MSN-15) represent organic poor sands. Hierarchical clustering of variables characterises four main interpreted clusters which are consistent with the PCA results. Mercury, S1, PAHs and pharmaceuticals, other than antibiotics, closely cluster, as do fine grain (clay/silt) %, TOC and bound hydrocarbons (S2), indicative of their close correlation (Fig. 4). Sand % is represented by its own individual cluster, far removed from fine grain, indicating their negative correlation. Antibiotic content represents an individual cluster but is closely branched with fine grain, TOC and bound hydrocarbons (S2), as demonstrated in the PCA.

Five short sediment cores collected close to south Singapore mainland within Singapore Straits contained a mix of pharmaceuticals that rank by concentration hormones> non-steroidal anti-inflammatory> antibiotics, corresponding in part to their physico-chemical properties (e.g. hydrophobicity, volatility) and also to quantity of source discharged into coastal waters. For example, caffeine and ibuprofen were observed in all five cores despite being highly soluble. The low but rising sedimentary accumulation of antibiotic compounds, azithromycin, clarithromycin, erythromycin_H_2O is of particular concern as there is a global need to reduce their presence in the environment to limit antimicrobial resistance and thereby maintain use in medical and veterinary science. Other factors such as post depositional decay and or mobility were inferred and may explain why propranolol, carbamazepine diclofenac were only detected at the surface in one core. The absence of region-specific multi-species ecological contaminant effect data (individual compounds, pharma group and mixtures) significantly hindered evaluation of potential impact on benthic biota. PAH pollution was more widespread than pharmaceuticals reflecting greater hydrophobicity and broader range of mainland source inputs and use as an anchorage for Port of Singapore. Nevertheless, these values were slightly lower than those reported in an earlier 2007 study indicating an improvement in sediment quality. Application of multiple source apportionment ratios and parent to alkylated profiles conferred mainly petroleum combustion sources with minor petroleum inputs. Only two samples from MSN15 exceeded (non-statutory) marine sediment quality guidelines (BaP, $\sum^{LMW}$PAH, $\sum^{HMW}$PAH) and these were at 25 and 35 cm depth. Overall, this study suggests that the groups of anthropogenic chemicals within Singapore sediments are shifting from traditional hydrocarbons (and presumably other persistent organics) to emerging contaminants of concern such as pharmaceuticals, personal care products and industrial additives should however, be recognised that these conclusions are based upon a small number of core sites covering a limited area of seabed (Fig. 1). Future marine sediment pollution studies should evaluate whether new emerging chemicals such as antibiotics are accumulating around the entire Singapore coast as well as conduct targeted geochemical surveys to define source transfer pathways.

CRediT authorship contribution statement

Christopher H. Vane: Funding acquisition, Formal analysis, Data curation, Conceptualization, Writing – review & editing, Writing – original draft. **Raquel A. Lopes dos Santos:** Methodology, Formal analysis. **Mark C. Kalra:** Formal analysis. **Vicky Moss-Hayes:** Formal analysis. **Olivia A. Graham:** Writing – review & editing. **Benjamin P. Horton:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

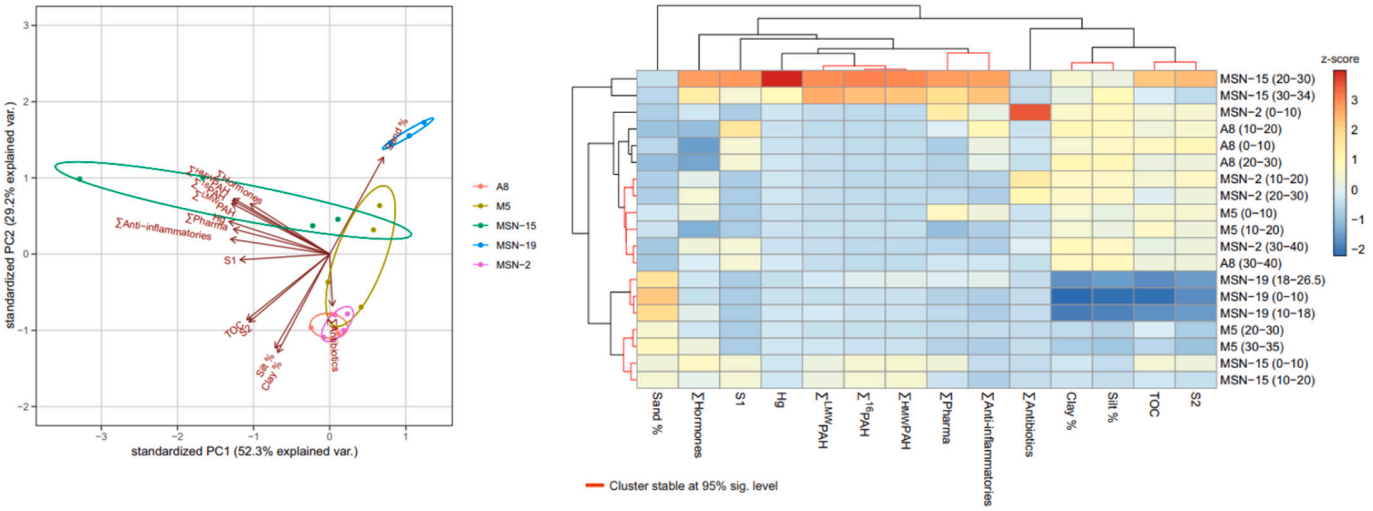

Fig. 4. Graphical-statistical evaluation of grouped chemical contaminant and ancillary data; a) principal component analysis (PCA); b) hierarchical cluster analysis (HCA).

the work reported in this paper.

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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.2025.118301.

Data availability

Data available upon request.

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