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Research article

The burden of emerging contaminants upon an Atlantic Ocean marine protected reserve adjacent to Camps Bay, Cape Town, South Africa

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ABSTRACT

The presence and levels of fifteen chemicals of emerging concerns, including five perfluorinated compounds (PFCs), two industrial chemicals, seven pharmaceuticals and one personal care product, were evaluated in biota, seawater and sediments obtained from near-shore coastal zone in Camps Bay, Cape Town, South Africa. Eight compounds were found in seawater, and between nine to twelve compounds were quantified in marine invertebrates, sediment and seaweed. Diclofenac was the prevalent pharmaceutical with a maximum concentration of 2.86 ng/L in seawater, ≥110.9 ng/g dry weight (dw) in sediments and ≥67.47 ng/g dw in marine biotas. Among PFCs, perfluoroheptanoic acid was predominant in seawater (0.21–0.46 ng/L). Accumulation of perfluorodecanoic acid (764 ng/g dw) as well as perfluorononanoic acid and perfluorooctanoic acid (504.52 and 597.04 ng/g dw, respectively) was highest in samples of seaweed. The environmental risk assessment carried out in this study showed that although individual pollutants pose a low acute and chronic risk, yet individual compounds each had a high bioaccumulation factor in diverse marine species, and their combination as a complex mixture in marine organisms might have adverse effects upon aquatic organisms. Data revealed that this Atlantic Ocean marine protected environment is affected by the presence of numerous and diverse emerging contaminants that could only have originated from sewage discharges. The complex mixture of persistent chemicals found bioaccumulating in marine organisms could bode ill for the propagation and survival of marine protected species, since many of these compounds are known toxicants.

1. Introduction

Evidence of the occurrence and impact of emerging contaminants (ECs) is increasing, resulting in global attention from researchers as well as regulatory bodies (Mijangos et al., 2019; Nieto et al., 2017; Wilkinson et al., 2017). Some of these chemicals are persistent, and their use is not regulated or monitored since they are still not listed in most environmental legislations. Persistence and fate of these contaminants in the coastal marine ecosystem are not fully understood (Chavoshani et al., 2020; Dey et al., 2019; Geissen et al., 2015; Sauvé and Desrosiers, 2014). Many of the studies reporting ECs in the marine milieu demonstrate that the impact of these chemicals are higher in the near shore coastal environment than further out to sea, as their presence is often linked to discharges originating from human activities along the coast (Branchet et al., 2021; Ghosn, 2019).

Perfluorinated compounds (PFCs), pharmaceuticals, endocrine disrupting compounds (EDCs) and personal care products (PCPs), are classed as ECs (Ebele et al., 2017; Montes-Grajales et al., 2017; Stroski et al., 2020; White et al., 2019). EDCs include industrial compounds such as flame retardants, phenolic products, pesticides, surfactants and plasticisers (Fauvelle et al., 2018; Geissen et al., 2015; Wilkinson et al., 2017). PFCs are used in the production of Teflon, as well as products that are stain resistant, and repel oil and water (Christensen et al., 2017). They are found in additives for motor oil, cleaning products, fire-fighting foams, cosmetics, ink and paints, medical equipment, adhesives and insecticides (Dai and Zeng, 2019; Lee et al., 2020). Pharmaceuticals include drugs such as analgesics, antibiotics, and hormones and PPCPs consist of cosmetics, fragrances, and detergents that are used on a daily basis (Ojemaye and Petrik, 2019a; Rivera-Utrilla et al., 2013; Weatherly and Gosse, 2017; Wyllie, 2015). Risks associated with the exposure to some of

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these chemicals for marine species and humans include thyroid disease (Ferrari et al., 2017) and low sperm quality (Selvaraju et al., 2021), alteration of steroidogenic pathways (Blanset et al., 2007), causing reproductive system disorders among women (Hunt et al., 2016), or cause feminisation (Jakimska et al., 2013).

Major routes of ECs found in marine environments originate from sewage effluents (in particular marine outfalls), aquaculture, agriculture, and disposal of waste (Lv et al., 2019; Ojemaye and Petrik, 2019a; Stroski et al., 2020; Wilkinson et al., 2022). levels and concentrations of ECs are normally in the range of nanogram to microgram per Litre in coastal waters (Álvarez-Muñoz et al., 2015; Bayen et al., 2014; Du et al., 2017; Kim et al., 2017; Lolić et al., 2015; Ojemaye and Petrik, 2022; Pal et al., 2014; Rodriguez-Narvaez et al., 2017; Stroski et al., 2020), and in sediments at of nanogram to milligram per gram in (dry weight) (Beretta et al., 2014; Moreno-González et al., 2015; Na et al., 2013; Ojemaye and Petrik, 2022; Xie et al., 2017). There is an increase in studies that focus on the presence and concentration of ECs in biota from marine milieu, with a focus on crustaceans, molluscs and fishes (Álvarez-Ruiz et al., 2021; Deere et al., 2020; Fliedner et al., 2020; Gilroy et al., 2017; Hallmann et al., 2016; Orbea et al., 2022; Rodil et al., 2019; Silva et al., 2017).

In the suburb Camps Bay on the Atlantic seaboard of the city of Cape Town, South Africa, there has in recent years been a concerted effort by the Camps Bay Ratepayers Association, among others, to draw city officials' attention to the problem of untreated sewage entering the bay. Camps Bay beach has a Blue Flag status, which indicates that its seawater should fall within Blue Flag norms for healthy seawater and beaches. It is therefore a highly sought-after international tourist destination which in summer it is famous for bathing. Camps Bay is an enclosed bay, with no manufacturing industry, and a suburb housing a populace of affluent citizens, and popular restaurants for tourists and bathers.

The detection of a wide range of ECs in the sewage sampled before discharge at the pump station located on the beach at Camps Bay has been well documented (CSIR, 2017). Some of these chemicals have the potential to bioaccumulate in sessile filter-feeder marine organisms, and at the lower food chain, and thus can be transported higher up in the food web (Ojemaye et al., 2020b). ECs are also known to bioaccumulate in regional biota from a previous study conducted in the nearby marine environment at Green Point (Petrik et al., 2017). A central question in disputes over the impact of the Camps Bay marine outfall has been if there is proven evidence of chemical pollution resulting from the sewer outfall in the marine protected reserve.

The study aimed to quantify the levels of fifteen compounds, five perfluorinated compounds, two industrial chemicals, seven pharmaceuticals and one PCP, in biota, seawater and sediment samples collected in Camps Bay. The purpose was to afford a holistic data set for the dispersion or lack thereof for ECs discharged with sewage into marine environment via the outfall in this bay, as well as ascertain the bioaccumulation of these chemicals in different trophic levels.

2. Materials and method

2.1. Site description

Camps Bay is approximately 850 m wide, 11 km south-west of Cape Town, having a suburban population density of 1,700/km^2. It is encircled by a rocky headland at Maidens Cove and facing Camps Bay Drive (CSIR, 2017) and is a sought after tourist destination, located at 33°57′00″S 18°23′00″E (Figure 1). The regions to the south and north of Camps Bay are comprised of pocket beaches of various sizes situated between rocky outcrops and shores. Sampling points, the discharge point of the marine outfall, as well as the position of the pump station, are shown in Figure 1. The Camps Bay marine outfall lies 700 m away from Maidens Cove beach and is located about 1.4 km from Camps Bay beach within the Table Mountain National Marine Protected Area (TMNMPA). The marine outfall discharges the sewage generated solely by the suburb itself (2.4 Ml per day) (CoCT, 2018; CSIR, 2017; Kretzmann, 2019), and the suburb is enclosed on three sides by mountains, cutting it off from the rest of Cape Town. There are no agricultural or industrial activities in this suburb.

2.2. Sample collection

The sampling activity was carried out in September 2017 during a period of drought. Three replicate samples of seawater (2 L each) were collected at 30 cm depth below the seawater surface (Figure 1): CS3 (at the shoreline), CS5 and CS6 (from the ocean), and stored in amber polypropylene bottles. Ice was used to preserve samples during the transportation to the laboratory. Cellulose filters (0.45 μm, 47 mm) were used to filter the samples and stored at 4 °C for five days till further extraction. MilliQ water was used as field blank and underwent the same procedure as the field samples.

Biotas collected were sampled from the intertidal zone from several rock pools in Camps Bay (sample codes: CS1-CS2, CS7-CS10 and CS13) (Figure 1 and Table 1).

Samples (biota) were collected by using a knife and a tong (stainless-steel), then wrapped in aluminium foil, at the same time sediment (250 g) were collected from points CS11 and CS12 (in triplicates), using a grab sampler (10 cm) and placed in polypropylene containers. Samples of marine biota and sediment were kept on ice during transportation to the laboratory. Invertebrates (removed from their shells), and seaweed were homogenised, then frozen at -80 °*C prior* to freeze-drying. Sediment samples were dried in air for 72 h at ambient temperature and preserved at -20 °C before sample analysis. The selection of analytes was based on earlier findings (Ojemaye and Petrik, 2019b; Petrik et al., 2017), including their detection in effluent (CSIR, 2017; Swartz et al., 2018), as well as from the compiled list of frequently prescribed drugs in the South Africa's health sector (Osunmakinde et al., 2013).

2.2.1. Materials and reagents

All compounds, 95% perfluoroundecanoic acid, PFUnDA; 97% perfluorononanoic acid, PFNA; 99% perfluoroheptanoic acid, PFHpA; 96% perfluorooctanoic acid, PFOA; 98% perfluorodecanoic acid, PFDA; 97% phenytoin, PHE; 99% bisphenol A, BPA; 97% sulfamethoxazole, SMX; 99% acetaminophen, ACT; 98% lamivudine, LA; 98% caffeine, CAF; 2-nitrophenol, 2NP; 98% diclofenac, DCF; 97% triclosan, TCS; 97% carbamazepine, CBZ; internal standards ($^{13}C_5$-PFNA, $^{13}C_4$-PFOA, sulfamethoxazole-d_4, $^{13}C_2$-PFDA, and acetaminophen-d_4) as well as the solvents used (acetonitrile, methanol and acetone) were obtained from Sigma-Aldrich (Modderfontein, South Africa) and BYMAZ Pty Ltd (Gauteng, South Africa). 6 cc, 500 mg and 200 mg Waters Oasis HLB Cartridges were supplied by Microsep, South Africa. MilliQ water from a MilliQ system (Millipore, Bedford, USA) was used throughout this study.

2.3. Preparation of sample and analysis

2.3.1. Water samples

Seawater extraction was done using previously reported methods (Petrik et al., 2017). In brief, samples (n = 3, 500 mL) were adjusted with HCl (1M) to pH 6. Upon conditioning of the SPE cartridges, samples were passed through separate SPE cartridges at a flow rate of 1 drop/second. Under low pressure, the SPE cartridges were then dried in the SPE manifold for 20 mins. The elution of the analytes was done using methanol (flow rate of 1 mL/min). Eluates were thereafter reduced to 2 mL under a gentle stream of N_2 gas. 10 μL, 1 ng/mL solution of internal standards (section 2.2) was added to each sample. The resulting solution was centrifuged, and finally passed through a 0.2 μm syringe filter and collected in a sample vial for analysis on liquid chromatography-mass spectrometry/mass spectrometry (LC–MS/MS).

2.3.2. Sediment and biota

Extraction was done using 10 g of freeze dried and ground sample (n = 9) in acetone/methanol (1:3 (v/v), 100 mL) by means of a soxhlet

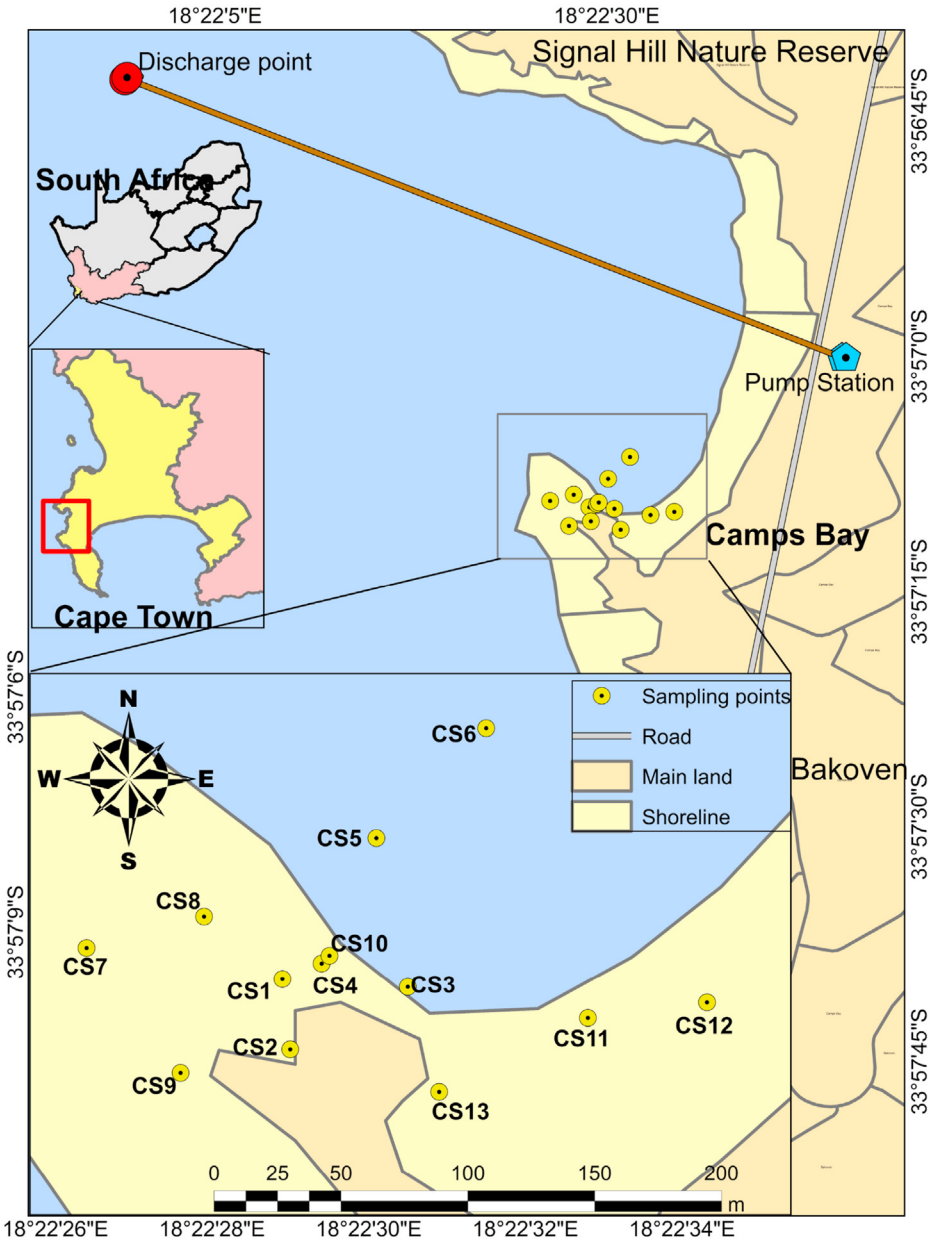


Figure 1. Sampling points for the Camps Bay study.

extractor, as previously reported (Ojemaye and Petrik, 2022; Petrik et al., 2017). Analyses of samples were done in triplicates. The extract resulting from the soxhlet extraction was subjected to SPE extraction following the procedure outlined for the seawater samples, using a flow rate of 1 mL/min (Detailed method in SI Section 1.1-1.2).

Table 1. Biota samples collected from the studied site.

Common name	Scientific name	No. of invertebrate	Weight of seaweed (g)
Limpets	*Cymbula granatina*	20	-
Sea urchins	*Parechinus angulosus*	15	-
Mussels	*Mytilus galloprovincialis*	30	-
Upright codium	*Codium fragile*	-	500
Sea lettuce	*Ulva* sp.	-	500

2.3.3. Instrumental analysis

Details concerning the LC-MS/MS analysis is described in SI Section 1.3. Briefly, PPCPs, PFCs and industrial chemicals extracted were analysed by an ultra-performance liquid chromatograph with sample manager and binary solvent manager (Waters Acquity UPLC system) coupled to a mass spectrometer (Xevo TQ-MS) equipped with an electrospray ionization source. Operation in multiple reaction monitoring mode was employed for the identification of compounds. An ACQUITY UPLC BEH C18 column (1.7 μm; 2.1 mm × 100 mm) (Waters, Mildford, MA, USA) with an ACQUITY BEH C18 VanGuard™ precolumn of dimension 1.7 μm; 2.1 mm × 5 mm at 50 °C was employed for separation.

2.4. Quality control and assurance

Limit of detection (LOD), linearity, limit of quantification (LOQ), precision, selectivity as well as accuracy of the procedure were carried out. Selectivity was done based on the compound relative retention time,

i.e. identifying analytes of interest using qualitative comparison of the retention time of the peaks found with the standard and comparing the corresponding spectra of the sample and analyte standard solutions. Precision was determined as a relative standard deviation (RSD) by evaluating five multiple injections of standard and sample, the calculated RSD were in the range of 3–12%. The linear correlation coefficient method (R^2) was used to evaluate the linearity, using seven-point calibration curves with concentration range 0.1–1000 ng/L, and the obtained R^2 values were >0.995. Accuracy, which was expressed as recovery percentages, was calculated by comparing the concentrations of analyte found in pre-spiked samples with post-spiked samples, recovery data are shown in Table 2. The evaluation of LOD and LOQ was done using a signal/noise ratio of 3 and 10, respectively. Blanks (procedural and field) were performed as controls for potential contamination in the laboratory and from field sampling. Work-up and analysis of blank samples were performed simultaneously with the field samples. No target compounds were present in the blanks.

2.5. Statistical analysis

Statistical Package for Social Sciences [(SPSS) IBM version 20 software] was used to analyse the data. Replication of data were expressed as mean ± SD.

2.6. Risk assessment

The risk assessment was evaluated using the risk quotient (RQ) method, which was calculated as the ratio between exposure estimate and effect estimate (US EPA, 2016). Using the worst-case scenario i.e., the highest measured environmental concentration was used, RQ was calculated for individual compounds found in seawater in Camps Bay marine environment (Equation 1).

$$RQ = \frac{exposure}{toxicity} = \frac{Measured\ \ Environmental\ \ Concentration\ \ (MEC)}{ecotoxicity\ \ endpoint} \quad (1)$$

where toxicity is the ecotoxicity endpoint (LC_{50} or EC_{50} or NOEC). In order to trigger the worst -case scenario (where the maximum concentration of the target contaminant was found) for the monitoring period, the highest measured concentrations were used to evaluate the RQ divided by an assessment factor (AF). For each contaminant, two approximate calculations were done with the toxicity data retrieved from the literature (Tables SI1 and SI2) for three different trophic representative levels of the ecosystem (vertebrate, invertebrate and algae) as well as the assessment factor (SI Table S3) suggested by the European Chemical Agency (ECB, 2003). The first estimation was for acute toxicity and the second was for chronic toxicity. For acute toxicity, when the RQ is >0.5 and above then the risk is considered high and for chronic toxicity when the RQ is greater than 1, then the risk is high.

3. Results

3.1. Occurrence in camps bay

LC-MS/MS parameters as well as the LOD and LOQ are presented in Table 2, and Figure 2 provides the concentration of compounds analysed in samples collected at Camps Bay. In this study, only bisphenol A and triclosan were below LOQ, and 2-nitrophenol was not found in any of the samples.

3.1.1. Seawater samples

Eight compounds were found in at least one of the seawater samples (PFDA, PFNA, PFOA, PFHpA, phenytoin, diclofenac, carbamazepine, acetaminophen), and two of these compounds (PFHpA and carbamazepine) were present in all the samples (Figure 2A). PFDA (2.44 ng/L) and diclofenac (2.86 ng/L) had the highest concentration and were also the most often detected compounds.

3.1.2. Sediment and beach sand samples

Ten compounds were found in at least one of the beach sand and sediment samples (Figure 2B). Compounds present in higher concentrations were diclofenac (134.9 ng/g dw), PFHpA (95.3 ng/g dw), PFDA (154.5 ng/g dw), PFNA (91.0 ng/g dw) and phenytoin (31.3 ng/g dw). Lamivudine was below LOQ in seawater. In all the sediment samples, ten compounds were detected, namely PFUnDA, PFDA, PFNA, PFOA, PFHpA, diclofenac, acetaminophen, carbamazepine, phenytoin, and caffeine.

3.1.3. Marine biota

In the marine biota samples (3 invertebrate and 2 seaweed species), 12 out of 15 analysed compounds were found. PFUnDA, PFHpA, PFDA, PFNA, phenytoin, and diclofenac (291.8 ng/g dw, 597.0 ng/g dw, 764.6 ng/g dw, 504.5 ng/g dw, 268.6 ng/g dw, and 357.5 ng/g dw, respectively) were the compounds with highest concentrations (Figure 2C). Lamivudine was only quantified in sea urchins, and it was below LOQ in the other biota samples.

3.2. Bioaccumulation

Bioaccumulation factors (BAFs) were expressed as the ratio of the concentration of a substance in an aquatic organism ($C_{organism}$) to its concentration in the surrounding water (C_{water}) (Agarwal et al., 2022; Kinney et al., 2008). A substance is considered to be "bioaccumulative'' when the BAF value is more than 5000 L/kg and "potentially bioaccumulative'' when BAF value is in the range of 2000–5000 L/kg in aquatic organisms (Na et al., 2013; Savoca and Pace, 2021). In this study, field derived BAFs were evaluated only for the ECs that were quantified in seawater and biota samples (Table 3). These values represent an estimation since they are not proportionate to equilibrium, mainly as a result of the high variation in concentrations present in seawater; yet they are consistent with calculated bioconcentration factors/BAFs.

The BAFs calculated in dry weight ranged from PFDA: 39000–313000, PFHpA: 325000–614000, PFNA: 256000–1577000, PFOA: 61000–151000, ACT: 65000–275000, DCF: 23000–125000, CBZ: 70000–214000 and PHE: 28000–93000 (Table 3).

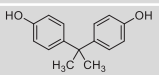
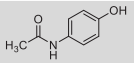
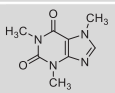
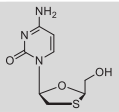
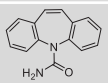
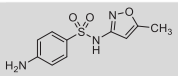
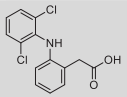
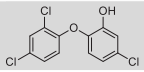
3.3. Environmental risk assessment

The risk assessment for Camps Bay marine environment was evaluated, and Figure 3 presents the risk posed by individual compounds to the selected trophic levels. The RQs of all the studied compounds were lower than 0.5, which showed that for acute risk, the three trophic levels (algae, fish, and invertebrates) from the site are not likely to be acutely at risk for individual compounds. Noteworthy, there was no difference in the risk level posed by the different ECs, since all the compounds pose comparable risk levels in the seawater. Regarding chronic risk, individual compounds posed a low risk (RQ < 1) across all three trophic levels in the seawater from Camp Bay.

4. Discussion

The contaminants identified in this study are pharmaceuticals for various therapeutic uses, PFCs and bisphenol A. Most of these contaminants have been reported for other marine environments (Caballero-Gallardo et al., 2021; Fang et al., 2012; Jiang et al., 2014; Kim et al., 2017; Liu et al., 2011; Lu et al., 2020). Pharmaceuticals, *viz.* diclofenac, acetaminophen, and carbamazepine, may enter sewage and thence be released into the marine milieu because of incomplete metabolism in humans, and consequent partial elimination from wastewater treatment plants. Compounds that have previously been reported in wastewater (Boxall et al., 2012; Cantwell et al., 2018, 2019; Lambropoulou and Nollet, 2014; Patel et al., 2019; Verlicchi et al., 2012) were also found in

Table 2. List of compounds analysed in Camps Bay by LC-MS/MS, the log (base 10) of the 1-octanol/water partition coefficient (Log k_{ow}), retention time (RT).

Compound	Molecular weight (g/mol)	Compound structure	Log k_{ow}	RT (min)	Transition Ion (m/z)	CE (eV)	LOD			LOQ			% Recovery		
							Seawater	Sediment	Organisms	Seawater	Sediment	Organisms	Seawater	Sediment	Organisms
PFHpA	364.06		6.86	6.82	363 to 319	15	0.03	0.04	0.06	0.08	0.13	0.18	96.5	97.5	99.8
PFOA	414.07		7.75	7.39	413 to 369	15	0.003	0.02	0.08	0.01	0.08	0.24	97.3	99.1	98.2
PFNA	464.08		8.64	7.88	463 to 419	15	0.01	0.05	0.08	0.02	0.14	0.23	98.0	98.9	100.4
PFDA	514.09		9.53	8.24	513 to 469	15	0.02	0.34	0.44	0.06	1.03	1.35	99.6	100.9	101.2
PFUnDA	564.09		10.42	8.57	563 to 523	15	0.04	0.53	0.84	0.11	1.61	2.55	97.0	98.5	98.3
Bisphenol A	228.29		3.43	5.87	227 to 212	28	0.01	0.03	0.44	0.05	0.08	1.35	96.2	96.9	97.0
Acetaminophen	151.16		1.10	2.01	152 to 110	15	0.02	0.32	0.32	0.07	0.98	0.98	98.1	99.3	99.8
Caffeine	194.19		-0.37	3.41	195 to 138	20	0.03	0.20	0.34	0.08	0.59	1.04	97.8	98.7	98.0
Lamivudine	229.26		-0.71	1.74	230 to 112	15	0.03	0.20	0.29	0.09	0.60	0.88	96.0	97.0	99.5
Carbamazepine	236.27		2.67	6.43	237 to 194	20	0.01	0.03	0.07	0.03	0.10	0.22	99.3	99.9	100.9
Phenytoin	252.27		2.52	6.18	253 to 182	15	0.27	0.37	0.37	0.81	1.12	1.12	99.0	98.4	98.9
Sulfamethoxazole	253.28		1.31	3.23	254 to 188	25	0.02	0.02	0.15	0.06	0.06	0.46	96.0	96.5	98.2
Diclofenac	296.15		4.06	6.72	296 to 250	15	0.03	0.23	0.33	0.09	0.71	1.01	98.6	99.4	101.3
Triclosan	289.54		5.17	9.09	288 to 36.80	10	0.02	0.07	0.27	0.08	0.22	0.81	95.9	96.7	95.5
2 nitrophenol	139.11		1.71	-	139 to 121	15	-	-	-	-	-	-	-	-	-

RT: Retention time CE: collision energy limit of detection (LOD) limit of quantification (LOQ).
ng/L for seawater and ng/g for sediment and biota.
PFHpA = perfluoroheptanoic acid, PFOA = perfluorooctanoic acid, PFNA = perfluorononanoic acid, PFDA = perfluorodecanoic acid, PFUnDA = perfluoroundecanoic acid.

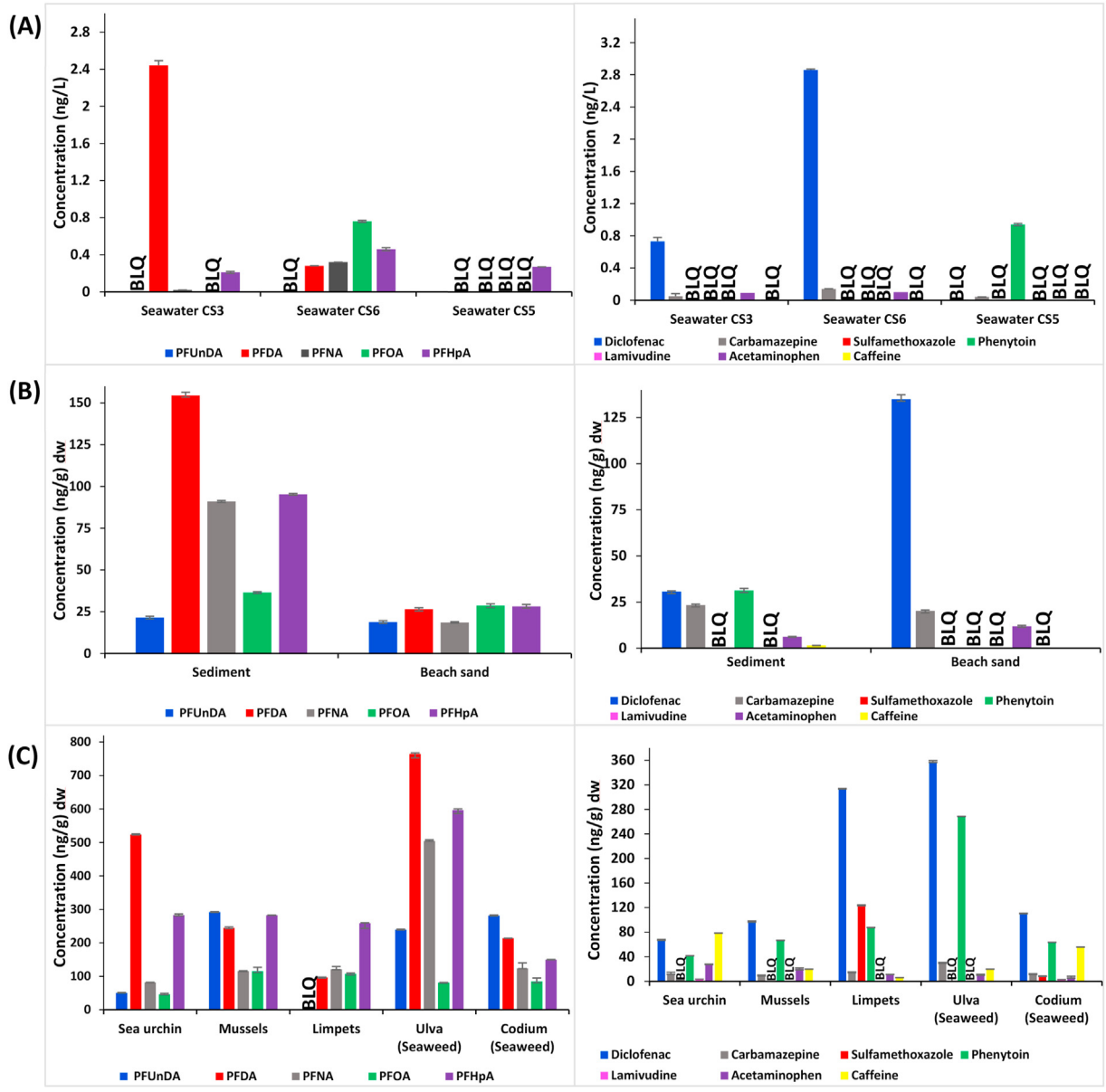


Figure 2. Concentration (mean ± SD) of contaminants in seawater (A), sediment (B) and biota (C), BLQ = below limit of quantification.

Table 3. Bioaccumulation factor (BAF) values of samples in dry weight, expressed as L/Kg. PFHpA = perfluoroheptanoic acid, PFOA= perfluorooctanoic acid, PFNA = perfluorononanoic acid, PFDA = perfluorodecanoic acid, PFUnDA = perfluoroundecanoic acid, ACT = acetaminophen, DCF= diclofenac, CBZ = carbamazepine

	BAF (L/Kg)				
	Invertebrates			Seaweeds	
Compounds	Sea-urchin	Mussel	Limpets	*Ulva* sp	*Codium fragile*
PFNA	256781	361031	376156	1576625	387187
PFHpA	614304	614130	562978	1297913	325000
PFOA	61000	151394	141328	106421	111184
PFDA	214725	100393	39582	313377	87631
ACT	275900	200400	111000	105000	65000
CBZ	87428	70142	107642	214357	86785
DCF	23591	34003	109804	124983	38776
PHE	44159	70691	93117	28265	67383

Table 4. Concentration of compounds in sewage effluent discharged into Camps Bay marine environment (from a CSIR Report (CSIR, 2017)) and in seawater samples (from the present study), reported as ng/L.

Compounds	Sewage at pump station (CSIR, 2017) ng/L	Seawater (this study) ng/L
Acetaminophen (paracetamol)	250000–970000	0.09–0.10
Carbamazepine	190–330	0.05–0.14
Diclofenac	630–1500	0.73–2.86

the seawater samples from Camps Bay and can only have been released into the bay through the marine outfall located in the bay, which pumps untreated sewage to the sea (CSIR, 2017). The concentration of the different contaminants quantified in all the samples of seawater was less than 3 ng/L. The concentrations of these compounds were lower compared to those found in sites from freshwater systems, usually located near wastewater outfalls (Cantwell et al., 2018, 2019; Gorga et al., 2013;

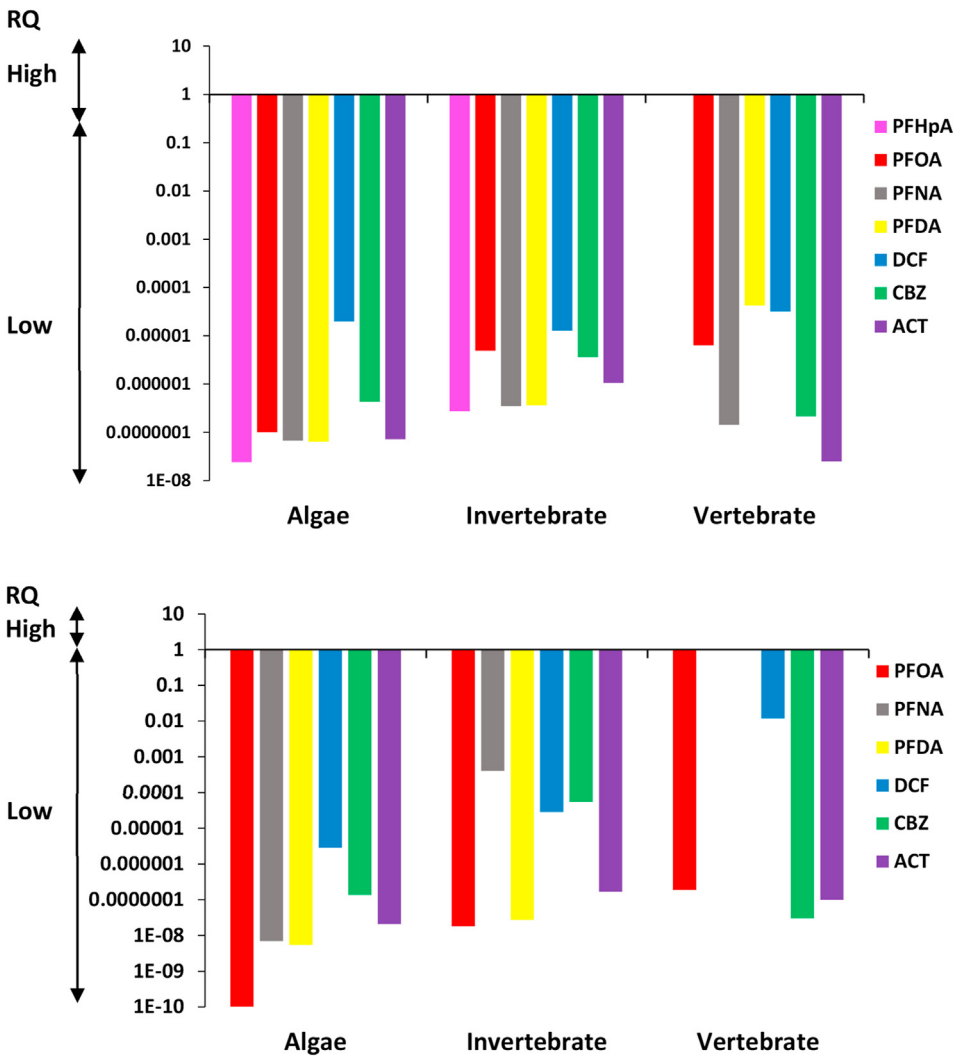


Figure 3. Estimated risk quotient (RQ) values of compounds for vertebrate, invertebrate and algae (top) acute risk (bottom) chronic risk.

Klosterhaus et al., 2013; Rodríguez-Navas et al., 2013; Scott et al., 2019; White et al., 2019; Wilkinson et al., 2022; Xie et al., 2015; Yang et al., 2011; Zhou and Broodbank, 2014), and comparable to levels found in studies from other estuarine and coastal/marine milieu (Birch et al., 2015; Fang et al., 2012; Knee et al., 2010; Marcotti-Murua et al., 2020; Stroski et al., 2020; Zhang et al., 2013).

The occurrence of these pharmaceuticals have also been reported in the Marine Bay of Singapore (Bayen et al., 2013), Cadiz bay, Spain (Biel-Maeso et al., 2018), the Baltic Sea (Björlenius et al., 2018), the Mediterranean Sea (Brumovský et al., 2017; Rodríguez-Navas et al., 2013), and Santos Bay (Brazil) (Pereira et al., 2016), although at a higher concentrations than those detected in the present study. Comparable concentrations of PFDA, PFNA and PFHpA were found in seawater from the Yellow Sea and Bohai Sea (Zhao et al., 2017) and Marseille bay (Fauvelle et al., 2018). On the other hand, higher PFCs concentrations were found in the present study compared to samples of seawater from the Yellow Sea (Zhou et al., 2018), Shandong peninsula coastal regions (Wan et al., 2017), Western Japan coastal waters and Osaka Bay (Beškoski et al., 2017) and Marseille Bay (Schmidt et al., 2019).

Over a sampling period of six months from March to Sept 2016, acetaminophen (paracetamol), diclofenac and carbamazepine were reported to be present in sewage effluent discharge from the pump station of Camps Bay, and it can be assumed that these concentrations being discharged into the bay remained relatively stable over the ensuing year (CSIR, 2017) (Table 4).

The levels in sewage of the painkiller acetaminophen, as well as carbamazepine and diclofenac were well above the levels detected in the seawater. Yet despite the purported sufficient dilution of the sewage and chemicals by the ocean, these contaminants were detected and quantified in the marine biota at levels considerably higher than found in the seawater, showing that dilution does not prevent bioaccumulation. The compounds however, were not uniformly diffused or dissipated in seawater as the dilution factor was not equivalent, which points to the irregular dispersion of these chemicals in the marine ecosystem. It also indicates that the rate of dispersion of those chemicals is associated with the properties of the chemicals, as they are not all equally hydrophilic.

The levels of ECs observed in an inorganic matrix, beach sand, compared to seawater show that these contaminants from sewage make regular landfall, giving rise to a build-up of chemical contaminants around the seashore, as the chemicals are not sufficiently washed off by enough clean seawater regularly to preclude accumulation. Sediments are functioning as a sink for all these contaminants (Ebele et al., 2017; Wan et al., 2017). This shows that the local discharge of chemically contaminated sewage in Camps Bay impacts the local coastline and that dilution in seawater does not prevent coastal contamination.

PFCs levels found in sediment samples from the present study were higher compared to levels reported in Jiaozhou Bay (Wan et al., 2017), the Bay of Bengal coast (Habibullah-Al-Mamun et al., 2016), Laizhou Bay (Zhao et al., 2013), the East China Sea and the Bohai Sea (Gao et al., 2014). The presence of PFCs and pharmaceuticals has also been reported

in Kagoshima Bay, the Pacific Ocean (Beškoski et al., 2017), and the Baltic Sea (Bayen et al., 2016; Siedlewicz et al., 2018), although at higher levels than those reported here. While the levels of carbamazepine diclofenac and PFCs reported in sediment samples from the Bering and Chukchi Sea (Lin et al., 2020), Baltic Sea (Siedlewicz et al., 2016), Bengal coast (Asaoka et al., 2020) and Kwazulu-Natal (Hlengwa and Mahlambi, 2020) were lower than the levels reported in this study.

There were variations in the concentration of each compound detected in the different species of biota. PFOA, diclofenac, PFNA, acetaminophen, PFDA, and PFHpA were found in all the biota samples. Bisphenol A and triclosan were below LOQ in biota as well as in sediment and seawater samples, while 2NP was not found in the different environmental matrices. Caffeine, commonly used as tracer for waste water discharge (Gonçalves et al., 2017), was also present in the marine organisms and seaweed, and it was not detected in the sediments or seawater, showing that even negligible levels in seawater could still cause bioaccumulation in these species.

The targeted PFCs and PPCPs have been detected in marine biota, with the exception of phenytoin (Álvarez-Ruiz and Picó, 2019; Li et al., 2012a, 2012b; Wille et al., 2011; Zhang et al., 2019). Similar levels of caffeine, diclofenac and carbamazepine as obtained in this study were also found in bivalves and algae from other studies (Ali et al., 2018; Martínez Bueno et al., 2013; Maruya et al., 2014; Mezzelani et al., 2020), while triclosan (Krogh et al., 2017) and acetaminophen (Wille et al., 2011) in mussels reported in other studies were found to be higher than levels observed in this study. In contrast, levels of PPCPs were lower than the ones found in previous research studies from Italy (Capolupo et al., 2017) and the Portuguese coast (Cunha et al., 2017; Rocha et al., 2018). Naile et al. (2013) and Hong et al. (2015) reported lower concentration of PFCs found in bivalves sampled at the west coast of Korea.

These results provide a reasonable demonstration of the impact of the sewage discharge in relation to ECs upon the marine reserve. The study was conducted between 2017 and 2019, which were the drought years in this region, during which this outfall was the only route for sewage discharged from the Camps Bay suburban area.

The detected ECs were also bioaccumulative, which demonstrates that the studied biota absorb these chemicals at a rate that is faster than the rate at which they are metabolized or excreted. The BAF variation observed in biota samples and the different levels of the investigated chemicals showed differences in interspecies' metabolic capacities (Ojemaye and Petrik, 2022; Roscales et al., 2019). BAFs for perfluorinated compounds in this study were comparable with previous findings (Dai and Zeng, 2019; Zhang et al., 2020).

Although the RQs of individual compounds were not high, they might still pose high toxic effects on marine organisms, causing adverse outcomes over the longer term. It should be noted that the method used to assess the impact of individual compounds on organisms ignores the effects from exposure to mixtures as well as the temporal dimension. Once the diverse analytes are taken up in the organisms, biotransformation may occur with production of secondary metabolites, with probable interactions, such as synergism or antagonism, between chemicals in the mixture. The compounds selected in this study are not the only compounds available in the evaluated seawater (Ojemaye et al., 2020a), neither will they exist just as the only compounds ecotoxicologically relevant. Therefore, the obtained results do not provide a complete picture of the seawater chemical load, but rather gives an assessment of the individual analysed compounds that were taken into consideration in this analytical survey.

5. Conclusion

The study showed that different classes of ECs present in sewage released into the marine environment via a marine outfall are present in Camps Bay seawater and sediment and significantly accumulated in marine invertebrates and plants. The levels of ECs found in marine invertebrates and plants in this marine protected environment show that the dilution of the sewage by the ocean as the means of dispersing the detected ECs is not adequate to prevent accumulation in marine organisms. The sub-nanogram per litre levels of these ECs in seawater did not prevent significant bioaccumulation in marine organisms. The detection of PFCs and PPCPs in Camps Bay biota and in the surrounding environment points out the significance of continued and regular investigation of coastal/marine milieus, as well as implementing adequate wastewater treatment before effluent discharge into the sea in order to maintain a healthy and functional marine ecosystem. Human exposure to these chemicals of emerging concerns through ingestion of seafood, contact, and accidental seawater ingestion is feasible. Even though the ecological risk posed to the three trophic levels is low, the elimination of these emerging chemical compounds is delayed in the organisms, as shown by the very high BAF results. The study conclusively shows that the daily introduction of sewage containing ECs via the marine outfall has increased the chemical burden impacting diverse species of biota. Therefore, there is a high likelihood of adverse effects accrual over time due to multiple toxicants' diverse interactions. It is recommended that future work considers predicting the effects of complex EC mixtures over time with toxicokinetic–toxicodynamic models.

Declarations

Author contribution statement

Leslie Petrik: Conceived and designed the experiments; Analyzed and interpreted the data;

Contributed reagents, materials, analysis tools or data; Wrote the paper.

Cecilia Ojemaye: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Lesley Green: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Daniela Pampanin; Magne Sydnes: Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interest's statement

The authors declare no competing interests.

Additional information

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