Human footprint on the water quality from the northern Antarctic Peninsula region

Cristina Postigo [a,b,*], Luis Moreno-Merino [c], Ester López-García [d], Jerónimo López-Martínez [e], Miren López de Alda [d]

[a] Technologies for Water Management and Treatment Research Group, Department of Civil Engineering, University of Granada, Campus de Fuentenueva s/n, Granada 18071, Spain
[b] Institute for Water Research (IdA), University of Granada, Ramón y Cajal 4, 18071, Granada, Spain
[c] Spanish Geological Survey CN IGME (CSIC), Ríos Rosas, 23, Madrid 28003, Spain
[d] Water, Environmental and Food Chemistry Unit (ENFOCHEM), Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/ Jordi Girona 18-26, Barcelona 08034, Spain
[e] Faculty of Sciences, Universidad Autónoma de Madrid, Campus de Cantoblanco, Madrid 28049, Spain

HIGHLIGHTS

- Human activity is impacting the chemical water quality in Antarctica.
- Ten contaminants of emerging concern (CECs) detected in fresh and marine waters.
- The spatial distribution of CECs in water is variable - environmental processes involved.
- Most relevant CECs: citalopram, clarithromycin, nicotine, venlafaxine, hydrochlorothiazide.
- Current measures are not effective to avoid CEC spread in Antarctica.

GRAPHICAL ABSTRACT
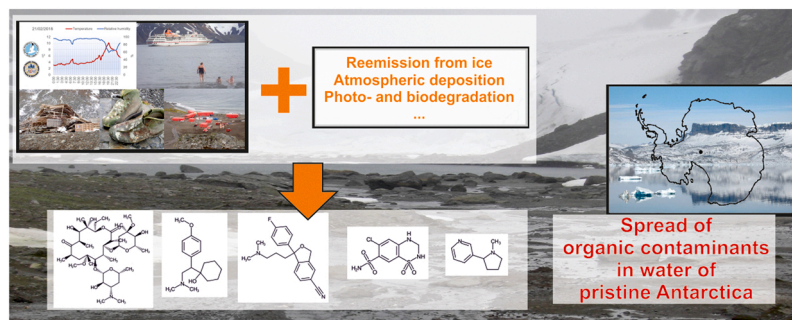
ARTICLE INFO

ABSTRACT

This study assessed the human footprint on the chemical pollution of Antarctic waters by characterizing inorganic chemicals and selected organic anthropogenic contaminants of emerging concern (CECs) in inland freshwater and coastal seawater and the associated ecotoxicological risk. Nicotine and tolytriazole, present in 74% and 89% of the samples analyzed, respectively, were the most ubiquitous CECs in the investigated area. The most abundant CECs were citalopram, clarithromycin, and nicotine with concentrations reaching 292, 173, and 146 ng/L, respectively. The spatial distribution of CECs was not linked to any water characteristic or inorganic component. The contamination pattern by CECs in inland freshwater varied among locations, whereas it was very similar in coastal seawater. This suggests that concentrations in inland freshwater may be ruled by environmental processes (reemission from ice, atmospheric deposition, limited photo- and biodegradation processes, etc.) in addition to human activities. Following risk assessment, citalopram, clarithromycin, nicotine, venlafaxine, and hydrochlorothiazide should be considered of concern in this area, and hence, included in future

* Corresponding author at: Technologies for Water Management and Treatment Research Group, Department of Civil Engineering, University of Granada, Campus de Fuentenueva s/n, Granada 18071, Spain.
  E-mail address: cristina.postigo@ugr.es (C. Postigo).

monitoring of Antarctic waters and biota. This work provides evidence on the fact that current measures taken to protect the pristine environment of Antarctica from human activities are not effective to avoid CEC spread in its aquatic environment.

1. Introduction

The Antarctic continent is usually thought of as the last great untouched wilderness on Earth. However, despite the remoteness and hostile environment of this area, with approximately 99.7% of the surface permanently covered with ice, it has not been free of anthropogenic activities. Explorers, sealers, and whalers started their activity in Antarctica in the early 19th century and scientific activities developed especially after the mid-20th century. Such activities had a profound impact on the biodiversity of Antarctic ecosystems due to the introduction of invasive species and overfishing, among other impacts [5,16]. The human presence, linked to research, tourism, and fishing activities, has noticeably increased in the last 65 years, and therewith, the anthropogenic impact on Antarctica, which includes the chemical pollution of the Antarctic pristine environments.

Residues of persistent organic pollutants (POPs), particularly the insecticide DDT (dichlorodiphenyltrichloroethane), were found in liver (up to 115 ng/g) and fat (up to 152 ng/g) of Antarctic penguins and seals in the early 1960 s [45]. Since then, numerous studies have reported the presence of POPs like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, dioxins, and furans in Antarctic marine foodwebs [2,15,22,30,31,40,42,44,47]. These chemicals are mainly transported southward over long distances through marine currents and atmospheric pathways [29,55], and they have been also reported to appear in various compartments of the Antarctic marine (seawater, sediments) [44] and terrestrial environments (lichens and soils, lake sediments) [23,50], and also in the snow [54], even without being directly used in the investigated areas.

Trace levels of organic contaminants of emerging concern (CECs) such as pharmaceuticals, psychotropic drugs, personal care products including UV-filters and fragrances, and preservatives like parabens, per- and poly-fluoroalkyl substances (PFASs), pesticides like pyrethroids, and a wide range of known endocrine disrupting compounds (e. g., benzotriazoles, organophosphate flame retardants, natural and synthetic estrogens, antimicrobials and alkyl-phenolic compounds) have been also found in Antarctica in recent years [14,15,19,20,24,26,46,49, 54]. Although long-range atmospheric transport processes of some CEC classes like fragrances [49] and PFASs [55] from their sources in mid-latitudes may occur, CEC presence in the Antarctic region is mainly associated with on-site research and tourism activities. Ca. 5500 people stay over the summer in 76 research stations spread throughout the territory [11]. These stations open either seasonally or year-round, and half of them are located on the northern Antarctic Peninsula and associated archipelagos. This Antarctic region is also the main objective of the tour operators. Tourist visits have doubled in the last decade. They accounted for 74,401 in the season 2019/2020 [28]. Consequently, and even though the Madrid Protocol was adopted in 1991 to protect the Antarctic Environment [43], the release of chemicals into the different Antarctic compartments due to transportation, energy production, and waste generation is unavoidable. Treated and untreated wastewater was indeed identified in previous studies as a relevant source of CECs [14,19, 20,24,26,46,49], and microplastics [10,25] in Antarctic surface seawater.

The research conducted on the occurrence of organic CECs in the Antarctic has been focused on continental freshwaters (snow melt or glacier drains, lakes, groundwaters, and streams) [14,20,24,26], wastewater discharges [14,19,20,24,26,46,49], snow [54], surface coastal seawaters [19,26,46,49], phytoplankton [15], and very few biota specimens (clams, sea urchins and fish) [19]. These studies aimed at performing preliminary assessments on the occurrence and

distribution of this type of pollutants in the Antarctic aquatic environment, identifying their potential primary sources, and assesssing, in a few cases [38], their potential ecotoxicological risks, including antibiotic resistance, and their bioaccumulation potential.

In this context, the main objective of the present work was to assess the human footprint on the chemical pollution of Antarctic waters by characterizing inorganic chemicals and selected organic anthropogenic CECs in inland freshwater and coastal seawater. For this, water samples were collected upstream and downstream of various research stations, at highly visited tourist areas, and in locations where no human impact was expected. Moreover, based on the CEC concentrations detected and their inherent chemical persistence, bioaccumulation, and toxicity properties, the ecological risk for exposed organisms was evaluated. The organic compounds selected for analysis included seven pharmaceuticals (acetaminophen, bezafibrate, diclofenac, citalopram, ibuprofen, hydrochlorothiazide, and venlafaxine), one antibiotic (clarithromycin), two stimulants (nicotine and caffeine), one UV-filter (benzophenone-1 or BP1), and one industrial contaminant (tolytriazole). The selection of CECs was based on their previous report in very few samples of water collected in the investigated area (this is the case for acetaminophen, clarithromycin, diclofenac, hydrochlorothiazide, ibuprofen, caffeine [24], BP1 [14], and tolytriazole [20]), their potential use as a wastewater tracer (caffeine [8] and nicotine [7]), non-existence of data in the Antarctic environment (nicotine and citalopram), their relatively high aquatic ecotoxicity potential (bezafibrate, citalopram, and venlafaxine) (ECOSAR tool [48]), their amenability to the simultaneous analysis by online solid phase extraction and liquid chromatography coupled to tandem mass spectrometry detection, and the previous experience of the authors in the multi-residue evaluation of CECs in water matrices. Moreover, some of the selected CECs, *viz.*, diclofenac, acetaminophen, ibuprofen, and clarithromycin, were recently identified as substances that may pose moderate and even high hazards to exposed organisms in freshwaters from Antarctica [38].

2. Materials and methods

2.1. Description of the investigated area and sample collection

A total of 38 water samples were collected on two islands of the South Shetlands archipelago, *viz.*, Deception Island (DI), and Livingston Island (LI) (Fig. 1), in January and February 2019. The sampling stations were located in areas impacted by anthropogenic activities (bases, camps, and tourism) and areas without apparent presence of humans and/or animals. Details on their location and potential degree of impact are provided in Table 1. Coordinates of the sampling stations are provided in Table S1 as Supporting Information.

Four out of the ten samples collected in DI were from Whalers Bay (3_D, 4_D, 5_D, and 6_D), one of the places in Antarctica most visited by tourists, and three samples were taken from the area surrounding the Spanish Base Gabriel de Castilla (1_D, 9_D, and 10_D). The remaining three samples in DI corresponded to areas not impacted in principle by human activities. Samples from LI were collected at the Hurd Peninsula, where Argentina Cove and the Spanish Base Juan Carlos I are located, and at the Byers Peninsula, an Antarctic Specially Protected Area (ASPA No 126) that can only be visited for scientific purposes. In the Byers Peninsula, some investigated sites are close to the temporary summer camp existing on the South Beaches (29_B and 30_B) (Table 1).

In total, 24 samples were collected from streams, 5 samples were taken from lakes or pools, 4 samples from springs, and 5 samples corresponded to coastal seawater.

Water samples for inorganic and organic compound analyses were collected in separate amber polyethylene terephthalate (PET) bottles (0.5 L). For the analysis of inorganic chemicals, sampling PET bottles were rinsed three times with the water to be sampled before sample collection and were headspace filled to avoid oxidation by atmospheric oxygen. In the case of organic chemicals, sampling containers were not pre-rinsed with the samples to avoid the potential absorption of less polar organic chemicals in the sampling material. No chemical preservatives were added to the water samples. Potential losses of the target organic chemicals were controlled by adding 20 ng of the isotopically labeled analogs to the sampled volume. All samples were stored and transported under controlled temperature conditions until analysis (4 °C ± 2 °C in the case of inorganic chemicals and −18 °C ± 2 °C in the case of organic chemicals).

2.2. Physical-chemical characterization of water

The electrical conductivity (EC), temperature, and pH of the water were measured in each sampling location using a WTW conductivity meter with a glass cell, and a WTW 320 pH meter (Xylem Analytics, Weilheim, Germany). The water alkalinity was also measured on-site using a Hach titrator kit (Test Kit model AL-DT) (Hach Lange GmbH, Düsseldorf, Germany). EC and pH of the water samples were also measured in the laboratory by electrometry following in-house developed and validated standard operation procedures.

2.3. Analysis of inorganic chemicals

The analytical techniques used for inorganic compounds are those recommended for drinking water according to the drinking water legislation in force in Europe at the time of analysis [17]. The methods used were capable of measuring at least concentrationsequal to the parametric values specified for the various inorganic parameters in the Council Directive 98/83/EC with a trueness, precision, and limit of detection of 10% of the corresponding parametric value, except for pH (trueness and precision values of 0.2 pH unit) and permanganate oxi-disability (trueness and precision values of 25%).

2.4. Analysis of anthropogenic organic micropollutants

High purity (>97%) analytical standards of the selected CECs and their isotopically labeled analogs were obtained from Sigma-Aldrich (Merck KGaA, Darmstad, Germany), Cerilliant (Round Rock, TX), Alsachim (llkirch-Graffenstaden, France), and Toronto Research Chemicals Inc (North York, ON). The list of analytes is provided in Table S2 as SI.

The determination of the target CECs was performed at the Institute for Environmental Assessment and Water Research from the Spanish National Research Council (IDAEA-CSIC) within six months from collection. The analyses were conducted with a fully automated method based on solid phase extraction and liquid chromatography coupled to tandem mass spectrometry detection (online SPE-LC-MS/MS analysis). For this, a Prospekt-2 sample processor (Spark Holland, Emmen, The Netherlands) connected in series with a 1525 binary HPLC pump and a Xevo TQ-S mass spectrometer (Waters, Milford, MA) was used. Briefly, 5 mL of the defrosted and centrifuged sample was extracted onto a HySphere Resin GP 10 cartridge (10 × 2 i.d. mm) previously conditioned with 3 mL of acetonitrile and 2 mL of water. After the sample load (at 1 mL/min), the cartridge was washed with either 1 mL of water in the case of freshwater samples or 5 mL of water in the case of coastal waters (at 5 mL/min) to remove matrix interferences in the LC-MS/MS analysis and avoid salt precipitation in the analytical system. All these steps occurred in the Prospket-2 extraction clamp and were assisted by a high-pressure dispenser unit. Then, the cartridge was mechanically placed in the Prospekt-2 elution clamp and connected to the HPLC pump. At this point of the analytical process, the mobile phase (water and acetonitrile, both with 5 mM ammonium acetate, at a flow rate of 0.3 mL/min and with a linear organic gradient) transferred the analytes from the cartridge to the chromatographic column (Purospher STAR RP-18e, 150 ×2.1 mm, 2 μm, Merck), and from this one to the MS/MS detection system. The ionization of the analytes was achieved using an electrospray source alternatively operated in positive and negative modes along the chromatographic run. The mass acquisition was done in the selected reaction monitoring (SRM) mode by registering 2 SRMs per target analyte and 1 SRM for each isotopically labeled analog. The compounds positively identified were quantified according to the isotope dilution method, which aids in correcting for potential losses that may eventually occur during storage and sample processing. The entire process was controlled with the SparkLink 3.10 (Spark Holland) and MassLynx 4.1 (Waters) software packages. Details of the online SPE-LC-MS/MS determination of the target analytes are provided in Table S2.

2.5. Quality assurance/quality control

Avoiding cross-contamination of the samples during collection and handling is essential for the reliable determination and quantification of trace levels of organic contaminants in water collected in pristine areas like Antarctica. This was ensured by wearing a mask and an unused pair of nitrile globes in each sample location and during sample handling in the laboratory. Moreover, all glass laboratory material was thoroughly cleaned with HPLC-grade water, ethanol, and acetone, and overnight heated at 350 °C before use. Method blanks, *i.e.*, HPLC water aliquots handled and processed like any water sample, were also analyzed within the sample batches (at the beginning and the end of each batch, after the calibration curve, and every three or four samples) to rule out potential
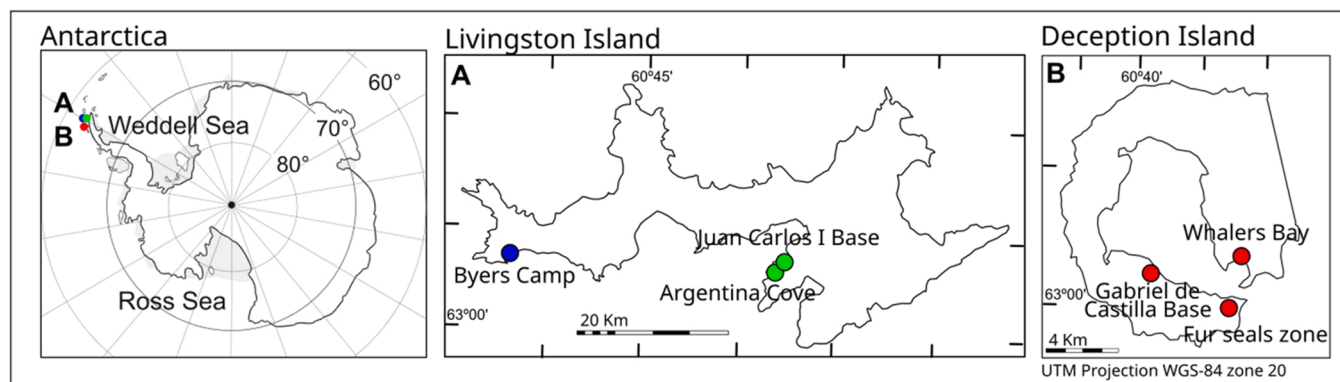

Fig. 1. Map showing the location of the sampling zones: Byers Peninsula (Byers Camp) and Hurd Peninsula (Juan Carlos I Base and Argentina Cove) in Livingston Island, and Deception Island (Gabriel de Castilla Base, Fur seals zone, and Whalers Bay). The location coordinates of the sampled points are provided in Table S1.

Table 1

Description of the sampling sites and degree of human (👤) and biological (🐦) impact in each site (scale from 1 to 5)*.

ID	Description of the sampling site	Degree of impact*
Deception Island: Gabriel de Castilla Base, Whalers Bay and Fur seals zone		
1_D	Zapatilla Lake (popular spot and with maintenance operations of the pumping system that supplies the base).	👤👤
2_D	Crater Lake, very rarely receives visitors.	
3_D	Whalers Bay (highly popular touristic area). Sample collected at a small stream fed by meltwater.	👤👤👤👤👤
4_D	Coastal seawater in Whalers Bay (close to the mouth of the stream sampled in location 3).	👤👤👤👤👤
5_D	Stream next to one of the collapsed houses in Whalers Bay.	👤👤👤👤👤
6_D	Coastal seawater in a beach area with natural hot springs where tourists bath.	👤👤👤👤👤
7_D	Stream with biological activity in the surroundings (no human or animal presence at the time of sampling).	🐦
8_D	Area with fur seals and without human activity (only science-related boat landing activities).	🐦🐦
9_D	Meltwater stream (upstream and at some distance from the base). Area with human activity when studies are conducted in the island. It may serve as a walking area for scientist due to its relatively close location to the base.	👤
10_D	Seawater in the discharge area of the Gabriel de Castilla base.	👤👤👤👤
Livingston Island: Juan Carlos I Base and Argentina Cove		
11_L	Water supplied to the Juan Carlos I base after being treated and stored.	
12_L	Meltwater from the glacier.	
13_L	Stream next to the base (sample collected downstream the base).	👤👤
14_L	Pool next to the base. It may receive direct runoff from the base area.	👤👤👤👤
15_L	Dumping area from the base to the sea.	👤👤👤👤
16_L	Stream sampled near its mouth into the sea.	👤👤
17_L	Small spring in the lower part of the base, with presence of mosses and lichens.	👤👤👤 🐦🐦🐦
18_L	Stream in the Argentina Cove (far from the base with very sporadic human presence, e.g., scientists passing by). Plastic packaging waste transported by sea and wind was found. On the coast, downstream from the sampling area, there is a notable presence of fur seals.	🐦🐦 👤
19_L	Stream near a moraine located upstream of the base.	👤👤👤
20_L	Stream on the glacier margin.	🐦
21_L	Stream with many algae that comes out of the glacier. There are no signs of biological activity. It should not be affected by human activity.	
22_L	Stream that collects the water of the plain at the foot of the glacier.	
23_L	Groundwater near the stream in the high plain. It may serve as a walking area for scientists due to its relatively close location to the base.	👤
24_L	Stream in the high plain. Sporadic visits from scientists. The surface water forms a large puddle with algae before it begins to flow. It may serve as a walking area for scientists due to its relatively close location to the base.	👤 🐦
Livingston Island: Byers Peninsula		
25_B	Stream located a few meters away from the camp. The sample was taken at the mouth of the stream.	👤👤👤
26_B	The lowest stretch of a stream at the beach. It is located to the west of the camp, close to a rocky hill.	🐦🐦
27_B	Stream that drains an area of moss located to the west of the camp.	🐦🐦
28_B	Seawater in the boat landing area located south of the camp. It is a dumping area of liquid waste from the camp.	👤👤👤👤

Table 1 (*continued*)

29_B	Pond area a few meters from the camp. Area frequently walked by people and used by birds.	👤👤👤 🐦🐦🐦 🐦🐦
30_B	Arrival of the stream to the camp area.	👤👤👤
31_B	Source of the stream that later reaches the camp. There is no human activity at present, but there is plastic and other waste buried (likely from past times).	👤
32_B	Stream with no apparent impact of the camp activities.	
33_B	Location upstream sample 32, with underground upwelling to the surface current.	
34_B	First stream to the east of the camp, sample collected near the mouth.	
35_B	Short stream. It is the second stream located to the east of the camp.	
36_B	Source of the stream sampled in location 34, set of abundant springs.	
37_B	Stream emergence located west to the camp and upstream. There should be no human influence but buried plastic debris have been seen.	
38_B	The second stream located to the east of the camp, emerging from a tunnel in the snow.	

*Degree of human impact was established according to the human presence in the sampling location (depending on the activities usually conducted in those areas: tourism/research/none). Degree of biological impact was established as a function of the animals and/or plants observed in the specific location at the time of sampling.

cross-contamination of the samples during handling and carry-over effects in the analytical system. Quality controls, *i.e.*, HPLC water aliquots fortified with the target compounds at a concentration of 10 ng/L were also analyzed throughout the sample batches.

The reliability of the organic contaminant concentrations provided is also ensured by the good performance of the online SPE-LC-MS/MS method used and the use of isotopically labeled analogs as surrogate standards. This method was validated in terms of linearity, accuracy (absolute and relative recoveries), precision (relative standard deviation of the results), and sensitivity. The method performance is summarized in Table 2 and discussed in detail in supporting information (Text S1).

The field instruments (pH and EC) were calibrated at least twice during each sampling day following the recommendations of their respective manufacturers. The thermometer was equipped with an individual factory-calibrated probe.

2.6. Environmental risk assessment

The risk that organic CECs may pose to exposed organisms was assessed with the hazard quotient (HQ) method. This approach compares the measured environmental concentration (MEC) with the Predicted No Effect Concentration (PNEC) for each compound [21]. Maximum and average concentrations were used as MEC to assess the worst-case and normal scenarios, respectively. To ensure maximum protection, half of the method limit of quantification (LOQ) was adopted for those compounds that were not detected or present at concentrations that could not be quantified. The PNEC refers to long-term exposure and was extracted from the NORMAN ecotoxicology database (lowest PNEC) [37]. The calculated HQ value suggests no risk (HQ<0.1), low risk (0.1 <HQ<1), moderate risk (1 <HQ<10), or high risk (HQ>10) for the organisms exposed to the individual investigated chemicals. Although this approach allows comparing the environmental risk of individual chemicals present in the environment, it does not consider the risk associated with the mixture. To address this aspect, an HQ was calculated for each sampling location (HQ_sample) by adding the individual HQs of the CECs present in each sample. This simple additive model is not free of limitations, as it does not consider other chemicals that may be potentially present but not analyzed and assumes that all chemicals have the same mode of action, which is not real. However, it is an acceptable approach to compare the environmental risk present in the different investigated locations.

Table 2

Method performance for the target analytes in surface and sea water in terms of linearity, accuracy, precision, and sensitivity.

	Linearity		Surface water								Sea water							
	Range (ng/L)	r²	Accuracy and precision*						Sensitivity		Accuracy and precision						Sensitivity	
			Absolute recovery (%)			Relative recovery (%) (RSD, %)			LOD (ng/L)	LOQ (ng/L)	Absolute recovery (%)			Relative recovery (%) (RSD, %)			LOQ (ng/L)	LOQ (ng/L)
			5 ng/L	50 ng/L	500 ng/L	5 ng/L	50 ng/L	500 ng/L			5 ng/L	50 ng/L	500 ng/L	5 ng/L	50 ng/L	500 ng/L		
Acetaminophen	2.5-2000	0.9925	9	9	14	120 (8)	109 (4)	109 (3)	0.50	2.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Benzophenone-1	1-2000	0.9900	52	66	72	105 (6)	136 (6)	138 (4)	0.30	1.0	49	65	76	126 (8)	163 (7)	162 (7)	0.30	1.0
Bezafibrate	0.1-2000	0.9912	208	181	140	117 (4)	103 (2)	102 (2)	<0.10	0.10	171	145	115	123 (5)	108 (2)	106 (1)	0.10	0.50
Caffeine	10-2000	0.9904	n.q.	100	99	n.q.	104 (1)	101 (1)	0.10	10	n.q.	86	81	n.q.	122 (4)	105 (2)	0.10	10
Citalopram	5-2000	0.9933	26	29	38	96 (5)	96 (2)	98 (2)	1.3	4.4	28	29	46	97 (4)	97 (5)	93 (2)	0.70	5.0
Clarithromycin	0.1-2000	0.9906	39	45	54	86 (6)	85 (2)	84 (3)	0.10	0.50	32	33	39	89 (4)	85 (4)	86 (1)	0.1	0.50
Diclofenac	5-250	0.9907	118	114	107	95 (9)	88 (3)	93 (3)	0.50	5.0	97	81	78	113 (16)	92 (3)	95 (2)	2.5	5.0
Hydrochlorotiazide	1-2000	0.9932	104	108	112	107 (7)	98 (5)	106 (3)	0.30	0.8	41	44	46	112 (15)	107 (6)	117 (5)	0.30	1.0
Ibuprofen	50-2000	0.9928	BLOD	62	50	BLOD	105 (35)	106 (16)	10	50	BLOD	46	43	BLOD	133 (29)	60 (38)	10	50
Nicotine	5-2000	0.9911	80	80	81	85 (7)	90 (3)	98 (3)	0.70	5.0	63	63	72	96 (19)	101 (6)	102 (3)	0.90	5
Tolytriazole	1-2000	0.9908	43	50	55	125 (8)	121 (2)	119 (2)	0.50	1.4	32	32	47	93 (11)	84 (4)	90 (3)	0.50	1.5
Venlafaxine	0.5-2000	0.9905	40	41	59	100 (2)	93 (1)	104 (0)	0.20	0.50	33	37	55	95 (2)	97 (2)	105 (1)	0.20	0.50

n.q – not quantified because of high background concentrations in the sample used in the validation study; n.a. – not analyzed; LOD – limit of detection, LOQ – limit of quantification. BLOD- below limit of detection.

*Absolute recovery was calculated by comparing the peak areas obtained in the LC-MS/MS analysis of pure standard solutions (n=3) with those obtained in the on-line SPE-LC-MS/MS analysis of surface (n=6) or sea water (n=6) fortified at equivalent concentrations. Relative recovery was calculated at each concentration level (n=6) by comparing the absolute recoveries obtained for the analyte and the isotopically labelled compound used for quantification. RSD: relative standard deviation of relative recoveries obtained at each concentration level (n=6).

As for the inherent capacity of a chemical to harm the environment, the hazard of the individual organic chemicals in terms of persistence, bioaccumulation, and toxicity (PBT) was also evaluated. For this, a variation of the PBT index described elsewhere [51] was adopted. First, each characteristic was scored with a value between 0 and 3 according to established criteria (Tables S3-S5), and then, the scored values were summed up. Thus, the PBT index would be 0 for a readily degradable, not bioaccumulative, and lowly toxic substance, and 9 for a very persistent, very bioaccumulative, and highly toxic substance. The persistence was assessed through the estimated biodegradability potential of the compound (using the BIOWIN and STPWIN models of the EPISuite tool) [48], the biodegradability assessment provided by the European Chemicals Agency [18] and the predictions obtained with the PROMETHEUS model available at the VEGA hub [3]. Since the ECHA assessment was not available for all target compounds and model predictions were dissimilar for some compounds, a final persistence score was obtained after scoring the results of the P score, the BIOWIN ultimate survey model, and the STPWIN model (Table S3). The bioaccumulation potential was scored taking into consideration the molecule octanol-water partition coefficient (average value of the experimental and predicted Log K_{ow} values provided by EPISuite [48], CompTox [52] and ChemAxon [9]) and experimental and predicted bioconcentration values (extracted from CompTox [52] and estimated with the PROMETHEUS model [3], respectively). Each of these properties, *i.e.*, Log K_{ow} and bioconcentration factor, were scored from 0 to 1.5 and scores obtained were added to obtain the final bioaccumulation score (Table S4). For ecotoxicity assessment, a four-step scale was established according to experimental (ECOTOX database [39] and ECHA brief profiles [18]) and predicted LC_{50} and EC_{50} values (using TEST [34] and ECOSAR [48] tools) for each of the three main aquatic trophic levels, *i.e.*, fish, daphnia, and algae. The same weight was given to all three trophic levels in their contribution to the final ecotoxicity score (Table S5).

2.7. Statistical analysis

The co-occurrence of organic contaminants and the potential connections between their presence with other water constituents and
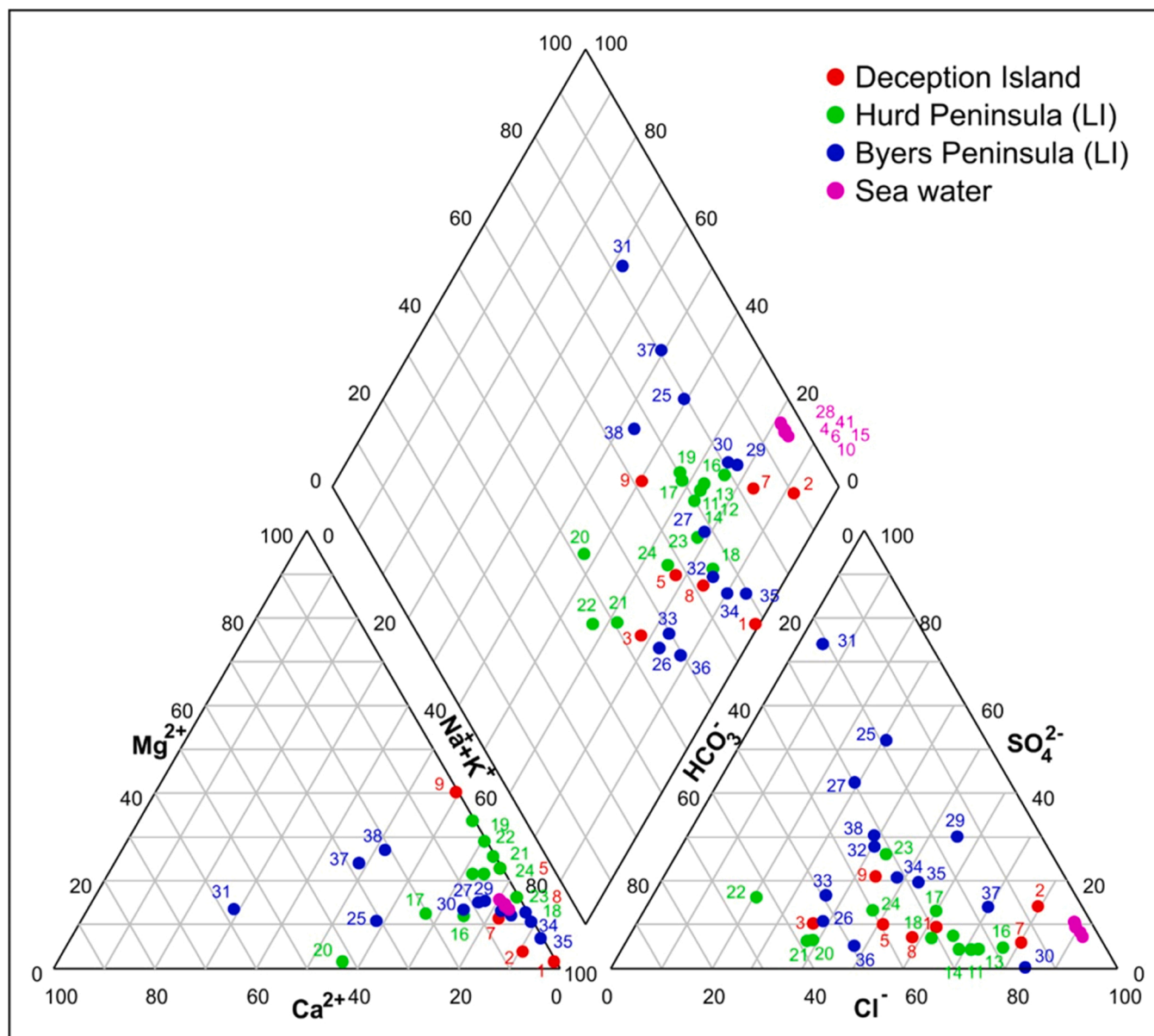

Fig. 2. Piper diagram showing the characteristic facies of the investigated waters grouped according to the sampling area.

characteristics were investigated through pairwise correlations using Spearman's rank test and a significance level of 0.05. Moreover, principal component analysis (PCA) was used to extract useful information from the data, *e.g.,* to identify potential contamination patterns. All statistical analyses, performed using the R statistical software interface R-Studio (R version 4.2.1), are described in detail as supporting information (Text S2 and S3). The variables used in statistics are summarized in Table S6. The R code used as well as the data are stored in a GitHub repository (https://github.com/cpostigo/Statistics_CECs-in-Antarctica).

3. Results and discussion

3.1. Hydrogeochemistry of the investigated area

The Piper diagram (Fig. 2) revealed the distribution of the hydrochemical facies occurring in the investigated area. The average values of hydrochemical parameters are shown in Table S6.

Cationic facies are very similar in the three investigated areas (Deception Island, and the Byers Peninsula and the Hurd Peninsula in Livingston Island), while anionic facies present a high variability. As for the cationic facies, all 33 freshwater samples investigated except five (9_D, 20_L, 25_B, 31_B, and 37_B) fell on a sodium type. The five exceptions belonged to either calcium-sodium or magnesium-sodium facies. As regards the anionic facies, 14 freshwater samples fell on a chloride type and 14 other samples fell on a chloride-bicarbonate type. Only five samples (25_B, 27_B, 29_B, 31_B, and 38_B), all from the Byers Peninsula, belonged to sulfate or chloride-sulfate facies. This could be attributed to the oxidation of the sulfur present in the parent rock when in contact with the atmosphere. This hypothesis is reinforced by the fact that all water samples associated with sulfate facies presented an acidic pH (Table S7).

Like the facies, the mineralization degree of the freshwater varied in the investigated areas. While all freshwater samples from Deception Island or the Hurd Peninsula in Livingston Island except 2_D showed very low mineralization (< 100 μS/cm), all freshwater samples from the Byers Peninsula in LI showed a mineralization level comparatively higher (200 μS/cm). The high EC value measured in sample 2_D (881 μS/cm), collected from Crater Lake in Deception Island, and the associated chloride-sodium facies could be explained by evaporative-concentration processes. The freshwater sample with the highest EC value was 27_B (983 μS/cm). No plausible explanation can be provided for this finding, because the stream sampled in 27_B is very similar in terms of morphology, materials, and amount of irradiation received to nearby streams where the water is much less mineralized.

The observed facies and the prevalence of highly soluble salts (*e.g.,* chloride and sulfate) among the most abundant ions found in the sampled waters can be explained by both the geological substrate and the effect of the sea spray aerosol. However, the latter has a weak effect as suggested by the weak water mineralization and the low values of the Cl/HCO₃ ratio (overall below 4). The highest value (8.3) is observed in the sample collected from Crater Lake (2_D). This reinforces the hypothesis that the high mineralization degree observed in 2_D origin from sea spray deposition and subsequent evaporative concentration. Overall, these results agree with the findings of previous studies conducted on the hydrochemistry of the Antarctic Peninsula freshwater [36].

3.2. Water characteristics and inorganic pollutants

The physical-chemical characteristics and content of inorganic pollutants in the investigated waters are summarized in Tables S7-S9. Most of the investigated waters presented total organic carbon (TOC) values very low (1.8 ± 0.6 mg/L) (Table S7), comparable to the TOC values measured in rainfall and oligotrophic lakes [32]. The TOC values found do not suggest anthropogenic or biological organic contamination of the waters. The water sample showing the highest TOC level (27_B, 4.01 mg/L) was collected from a stream that drains a moss-rich area.

The pH value of the water in the investigated locations ranged between 5.39 and 8.15 (Table S7), and this parameter was inversely correlated with NO_3^- ($\rho = -0.63$, p-value <0.05) and SiO_2 concentrations ($\rho = -0.62$, p-value <0.05) (Fig. S1).

The inorganic indicators of biological activity (NH_4^+, NO_2^-, NO_3^-, PO_4^{-3}) did not show a significant and/or relevant correlation among them or with the degree of human and biological impact (Fig. S1). In the case of phosphorous, this and the low concentrations measured in all samples suggest its geogenic origin. NO_3^- concentrations in samples 37_B (56 mg/L), 26_B (15 mg/L), and 7_D (11 mg/L) were much higher than in the remaining investigated samples (n.d-4 mg/L) (Table S8). While the high NO_3^- values measured in samples 7_D and 26_B may be associated with sporadic contamination events generated by animal presence, this should not be the case in location 37_B (upstream of the camp, where no biological activity was observed). In this location, additional NO_3^- sources should not be discarded because buried plastic debris was found.

Sample 30_B was the only sample with measurable levels of NH_4^+ (8.4 mg/L) (Table S8). Since other nitrogen species were not detected, and the sample was collected before the stream runs through the camp area, this value is associated with the very sporadic presence of birds in the area. The absence of NH_4^+ in the remaining samples and NO_2^- in all samples suggests the prevalence of oxidative conditions in all investigated locations.

Positive and strong relationships ($\rho > 0.81$, p-value <0.05) were found between EC and total dissolved solids (TDS), Na^+, Ca^{+2}, Mg^{+2}, Cl^-, SO_4^{-2}, and HCO_3^-; between TDS and Na^+, Ca^{+2}, Mg^{+2}, Cl^-, SO_4^{-2} and HCO_3^-; between Na^+ and Ca^{+2}, Mg^{+2}, Cl^-, SO_4^{-2} and HCO_3^-; between Ca^{+2} and Mg^{+2} and Cl^-; and between Mg^{+2} and Cl^- (Figs. S1 and S2). While in some cases, the increased levels of these parameters are attributed to the seawater impact (25_B, 26_B, and 35_B), in other locations this aspect can be associated with evaporative processes (2_D) or natural geologic processes (27_B, 30_B, 31_B, 38_B).

3.3. Organic micropollutants

The occurrence of organic micropollutants in the investigated water samples is shown in Fig. 3 and summarized in Table 3, while detailed data are provided as supporting information (Table S10). The most ubiquitous organic micropollutants were tolytriazole and nicotine, with frequencies of detection of 89% and 74%, respectively. Acetaminophen, ibuprofen, and bezafibrate were not detected in any water sample, while the remaining organic CECs were present in 3 – 55% of the samples analyzed.

The highest average concentrations were observed for benzophenone-1 (51 ng/L), followed by citalopram (29 ng/L), caffeine (25 ng/L), nicotine (21 ng/L), and clarithromycin (19 ng/L). Hydrochlorothiazide, tolytriazole, and venlafaxine presented average concentrations between 3.5 and 6 ng/L. Previous studies reported similar or even slightly higher concentrations of these compounds in surface water and glacier drain from other locations of the South Shetland Islands archipelago, *e.g.,* tolytriazole (5.37–14.68 ng/L) [20], benzophenone-1 (below 2.8 and up to 390 ng/L) [14], caffeine (below 0.66 and up to 323 ng/L), hydrochlorothiazide (13–181 ng/L), and clarithromycin (16–20 ng/L) [24]. The occasional presence of diclofenac was also reported on Seymour Island [24], one of the sixteen islands around the tip of the Antarctic Peninsula; however, the concentrations found (77 ng/L and 7761 ng/L) were 10 and 1000 higher than the one measured in this study (7 ng/L). Contrary to our findings, Gonzalez-Alonso et al. [24] measured relevant concentrations of acetaminophen (25–38 ng/L) and ibuprofen (37–974 ng/L) in surface waters. All detected CECs, except for venlafaxine, a CEC scarcely investigated in this polar area, have been previously found in wastewater discharged into the Antarctic environment at concentrations always above the ones found in natural streams and coastal seawater in this study [14,19,20,24,26,46]. This points out wastewater as a relevant source of CECs in Antarctica.
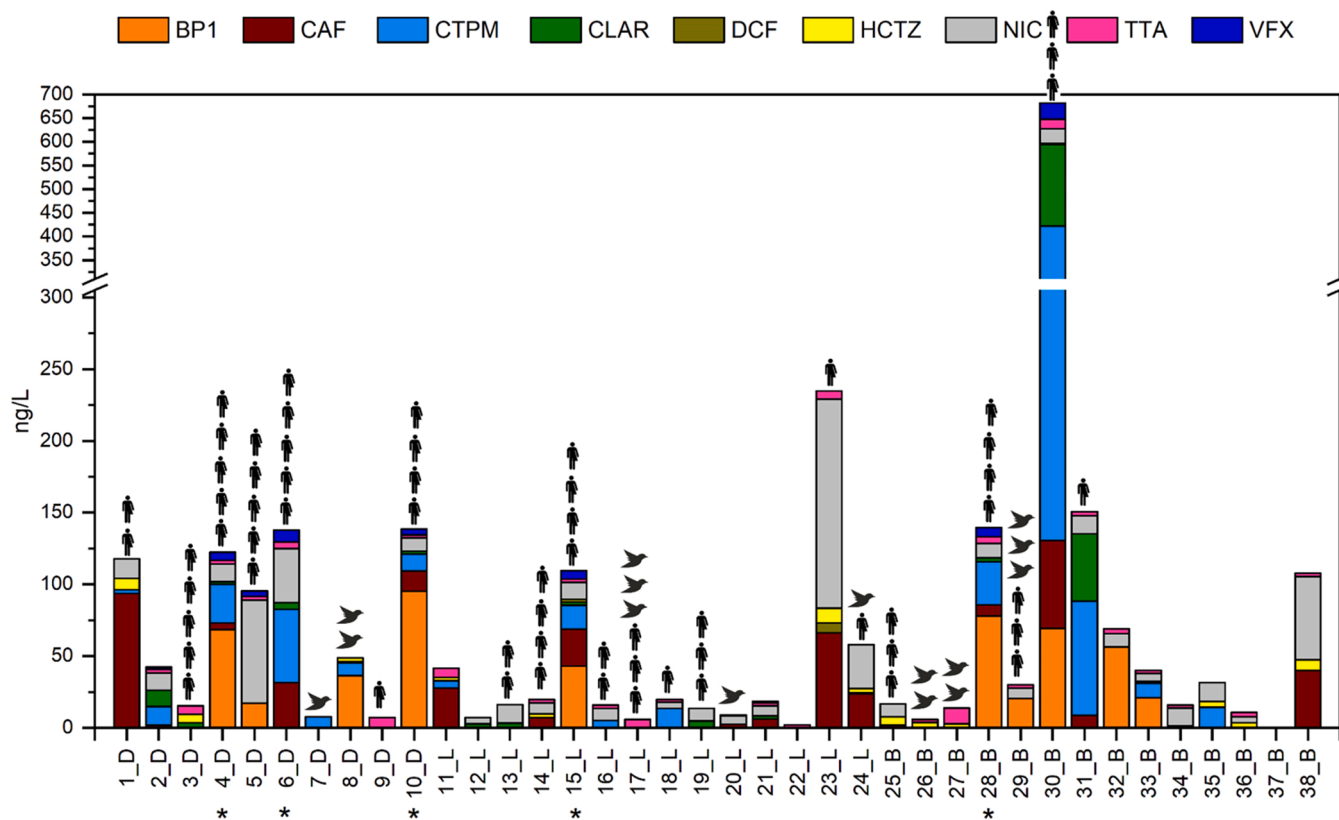
Fig. 3. Cumulative concentrations (ng/L) of the investigated organic CECs in the water samples were analyzed and estimated human and biological impact in each sampling location (seawater samples are indicated with an asterisk). BP1: benzophenone-1, CAF: caffeine, CTPM: citalopram, CLAR: clarithromycin; DCF: diclofenac, HCTZ:hydrochlorothiazide, NIC: nicotine, TTA: tolytriazole, VFX: venlafaxine.

Table 3
Frequency of detection (FD, %) and concentration (ng/L) of the selected organic CECs in the investigated area of Antarctica.

	FD. (%) (n = 38)	Freshwater Concentration (ng/L)		Seawater Concentration (ng/L)		PNEC ** (µg/L)
		Range	Average*	Range	Average*	
Acetaminophen	0					134
Benzophenone-1	26	17–69	37	0.2–95	57	1.71
Bezafibrate	0					2.3
Caffeine	45	1.7–94	28	4.6–32	17	1.2
Citalopram	55	< 4.4–292	29	12–51	27	16
Clarithromycin	39	0.7–173	25	2.0–4.4	2.8	0.12
Diclofenac	3	7.1				0.63
Hydrochlorotiazide	50	< 0.8–10	3.7	1.8		8.38
Ibuprofen	0					1
Nicotine	74	4–146	22	9.3–38	16	5.45
Tolytriazole	89	0.7–20	3.6	2.1–4.6	3.2	8
Venlafaxine	32	0.3–35	6.8	4.1–8.3	6.1	0.038

*LOD values were not considered in the calculation of average values, and LOQ values were considered as LOQ/2
* *Lowest predicted no-effect concentration in freshwater (extracted from the NORMAN ecotoxicity database). The PNEC in marine water is 10 times lower than the PNEC in freshwater.

After performing pairwise correlation tests, the degree of human impact in each location (estimated on-site through direct observation) resulted to be positively related to the individual concentrations of clarithromycin, nicotine, and venlafaxine ($\rho = 0.36$–0.43, p-value <0.05), and the total concentration of organic contaminants, whereas the degree of biological impact seemed to be negatively related to nicotine concentration ($\rho = -0.39$, p-value <0.05) (Fig. S1).

Caffeine and nicotine concentrations were positively related ($\rho = 0.57$, p-value <0.05) (Fig. S1), and both of them showed a strong positive relationship with the total concentration of CECs in the water samples ($\rho = 0.72$ and 0.74, p-value <0.05), which is consistent with the fact that they are all substances of anthropic origin. Caffeine and/or nicotine are the major contributors to the total CEC concentrations in many locations with some degree of human impact like 1_D, 23_L, and 24_L among others (Fig. 2). The presence of these contaminants in location 38_B, where no human activity occurs, could be attributed to wind transport, as the wind blows to this area from the camp. Thus, as previously suggested in the peer-reviewed literature [7,8], these chemicals seem to be suitable as markers of anthropogenic impact. Consumption of clarithromycin, citalopram, and venlafaxine seemed to be also associated ($\rho = 0.52$–0.55, p-value <0.05) (Fig. S1). Such relationships can be also identified in the network plot of the correlation

data frame (Fig. S2). Overall, the occurrence of CECs was not directly related to other water inorganic constituents and water parameters (Fig. S1). Significant and relatively strong correlations ($\rho = 0.53$–0.56, p-value <0.05) were only observed between citalopram and EC, TDS, and sodium and chloride concentrations (Fig. S1). This may suggest a longer half-life of this chemical in seawater than inland freshwater; however, this is only a speculation, because there is no additional evidence or data to support this hypothesis. Venlafaxine was also positively related to potassium, arsenic, manganese, and uranium concentrations ($\rho = 0.50$–0.59, p-value < 0.05) (Fig. S1). In this case, however, no plausible explanation for this relationship can be provided.

All seawater samples presented a similar contamination profile of CECs (BP1 in all samples except in 6_D > citalopram, nicotine, and caffeine > venlafaxine > tolytriazole) and similar total CEC levels (110–140 ng/L) (Fig. 3; Table S10). This suggests a stable pollution profile in coastal seawater. Contrarily, the contamination profile in surface waters in terms of both quantity and composition varies from site to site, which is attributed to the vicinity of pollution sources (anthropogenic impact) and the role of environmental factors (reemission from ice, atmospheric deposition, photodegradation, and biodegradation processes, etc.).

The highest cumulative concentration of organic CECs in streams was observed at the Byers Peninsula (LI) in sample 30_B, which corresponds to water collected from a stream upon its arrival at the camp and downstream of a location where buried waste and plastic were found (31_B). The levels of CECs found in this sample (682 ng/L) are 11 times higher than the average levels found in all investigated freshwater samples (60 ng/L). On the other side, only one location was free of the investigated organic CECs (37_B). This location is also free of human

activity. Overall, although with exceptions (1_D, 3_D, 14_L, 17_L, 19_L, 23_L, 25_B, 29_B, 31_B, 38_B), the lowest total CEC concentrations were found in locations with no or low human activity (Fig. 3). The low total CEC concentrations found in locations with strong human activity may be justified by dilution processes with snowmelt (3_D) or continuous and relatively high flows of the sampled streams (25_B) and by the collection of grab samples that may not catch contamination events such as the visit of scientists or groups of tourists. On the other end, the high concentrations found in locations with weak human activity may be explained by human presence in the recent past (31_B) or may reflect the contamination status at that point in time (23_L and 38_B). Unintended contamination of the samples with nicotine and caffeine is discarded since appropriate measures were adopted during sample collection and manipulation to avoid it (use of a new pair of gloves for each sample and cover of nose and mouth). In addition, none of the persons involved in water sampling and CEC analysis were smokers.

Additionally, the existence of potential contamination patterns of organic CECs and their spatial distribution in the investigated area was statistically explored through PCA (Text S3). The four first principal components (PCs) could explain 96% of the data variance (Fig. 4, Table S11). The PCA did not reveal geographically differentiated contamination patterns (see PCA biplots in supporting information, Fig. S4). Several organic CECs contributed to the contamination patterns established by each PC. In the case of PC1, which explains 59% of the variance, the sum of all analyzed CECs and all detected pharmaceuticals except hydrochlorothiazide contributed to the variability observed. On the other hand, nicotine caffeine and hydrochlorothiazide are the main contributors to the contamination patterns captured by PC2 (associated with samples 23_L, 1_D, and 38_B) and PC3. In PC2 (25% of the variance)
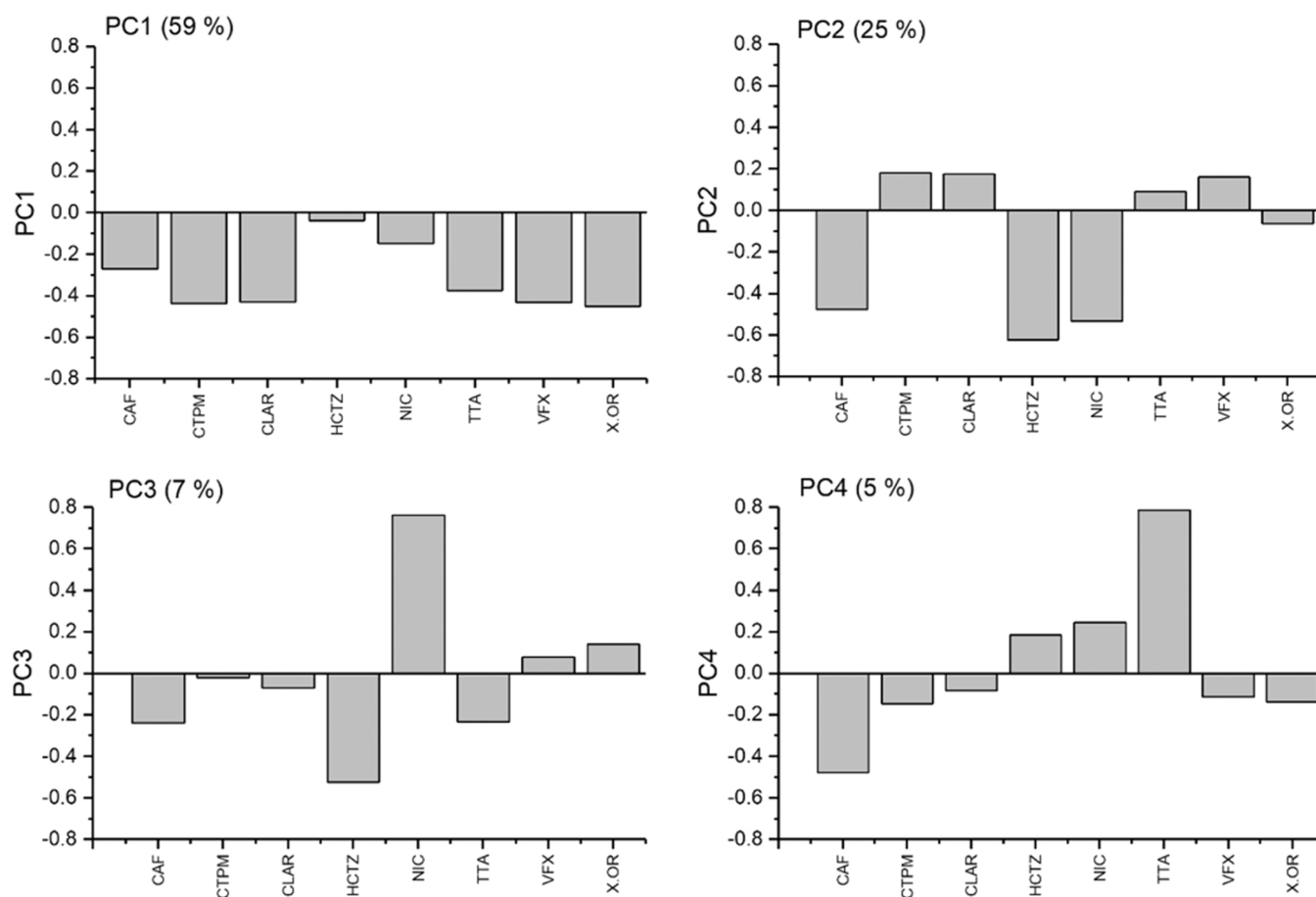

Fig. 4. Amount of variance explained by each PC and loading plots along the first four PCs. CAF: caffeine, CTPM: citalopram, CLAR: clarithromycin; HCTZ:hydrochlorothiazide, NIC: nicotine, TTA: tolytriazole, VFX: venlafaxine, X.OR: total concentration of CECs.

these three variables were related, while in PC3 (7% of the variance) nicotine was not correlated with either caffeine or hydrochlorothiazide. PC4 describes a contamination pattern driven by tolytriazole and caffeine (not correlated) (Fig. 4). The biplot of the two first PCs (explaining 84% of the variance) depicts a similar contamination pattern among samples 11_L, 27_B, 31_B, and all seawater samples (4_D, 6_D, 10_D, 15_L, 28_B). In the case of seawater samples, this can be attributed to the same origin and degradation processes; however, no plausible explanation can be provided for the similarity observed in freshwater samples since they belong to different hydrogeological and geographical environments (sample 11_L is the water supplied to the Juan Carlos I Base, while samples 27_B and 31_B are independent streams in Byers Peninsula). Except for samples 1_D, 23_L, 30_B, and 38_B, all samples seem to belong to one unique group in terms of organic contamination.

The potential occurrence in biota samples from the Antarctic region of the CECs detected in this work has been hardly explored, since most of the studies have focused on the bioaccumulation of persistent organic pollutants (*e.g.*, PAHs, flame retardants, organochlorine pesticides, or PCBs) [4,33,35,40,41,53]; and PFAS [1,27]. From the CECs found in water in the present study, only BP1 has been investigated in biota samples from Antarctica (clams, urchins, and fish collected in the coastal waters close to McMurdo Station in Ross Island) [19]. Although BP1 was not found in the investigated organisms, another widely used UV-filter, namely oxybenzone (BP-3), was found in all clamp samples analyzed (9.2–112 ng/g dry weight), and in a few of the fish and urchin samples analysed (slightly lower concentrations). Preservatives like methyl paraben and propyl paraben, the natural estrogen 17β-estradiol, the synthetic estrogen 17α-ethynyl estradiol, the faecal steroid coprostanol and the surfactant 4-t-octylphenol were also found in these biota samples [19]. A wide-scope screening of organic contaminants in phytoplankton cells from Port Foster Bay (DI) revealed the presence of five personal care products (including BP3), ten biocides, and 40 pharmaceuticals among other chemicals [15]. However, there is no overlap among the CECs found in the present study and the ones found in the phytoplankton, which can be attributed to insufficient bioaccumulation potential of these CECs in the phytoplankton cells or differences in the analysis (*e.g.*, the sample extraction protocol, or the extent of matrix effects in the non-target approach with Fourier-transform ion cyclotron-resonance mass spectrometry applied by Duarte et al. [15] and the target method based on LC-MS/MS applied in this work).

3.4. Risk assessment

HQs were calculated for the investigated organic CECs using the maximum (the worst-case scenario) and average (normal scenario) concentrations found in fresh and seawater samples as MEC (Table 3, Fig. 5). In the case of acetaminophen, bezafibrate, and ibuprofen, which were not detected in any sample, half of their corresponding LOD in each matrix was used as MEC in the worst-case scenario. The PNEC values for each organic CEC in fresh and seawater were extracted from the NORMAN ecotoxicology database and are summarized in Table 3.

According to calculated HQ values, the individual concentrations measured for most of the target CECs are not likely to pose a risk to exposed aquatic organisms in freshwater (HQ < 0.1). A moderate risk could only be expected for clarithromycin in the worst-case scenario (HQ=1.44), while adverse effects cannot be fully dismissed for this antibiotic in the normal scenario (HQ=0.21) and venlafaxine in both scenarios (HQ=0.18 and 0.92). This could be attributed to their very low PNEC values (0.038 and 0.12 µg/L for venlafaxine and clarithromycin, respectively) and the high concentration of clarithromycin in freshwater (173 ng/L). In seawater and both investigated scenarios, a low risk (0.1 < HQ < 1) could be anticipated for benzophenone, caffeine, and clarithromycin, and a moderate risk for venlafaxine. Such findings derive from their very low PNECs in seawater (between 0.0038 and 0.171 µg/L).

The overall hazard quotient of the investigated samples (HQ_{sample}) was below 0.1 in 76% of the cases. The calculated HQ_{sample} values suggested a low ecotoxicity risk in three samples (5_D, 8_D, and 31_B) and a moderate risk in six samples (all five seawater samples and sample 30_B). The moderate risk observed in all seawater samples is attributed to the low PNECs of the organic CECs in this matrix, which are ten times lower than their corresponding PNECs in freshwater. The main
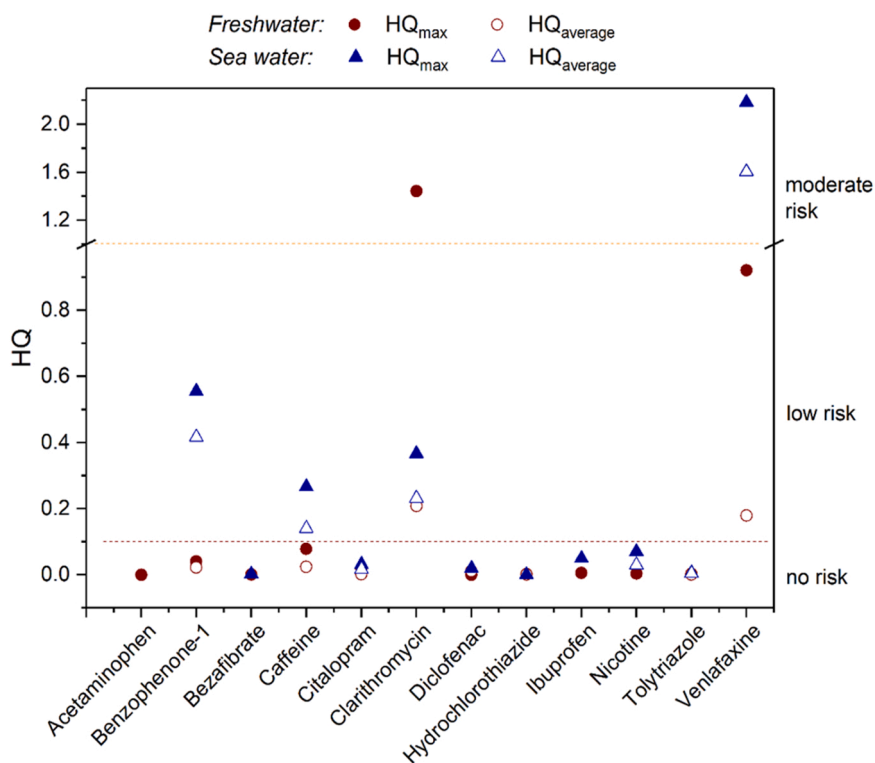

Fig. 5. HQ of each target organic contaminant in freshwater and seawater in the worst-case (HQ_{max}) and normal ($HQ_{average}$) scenarios.
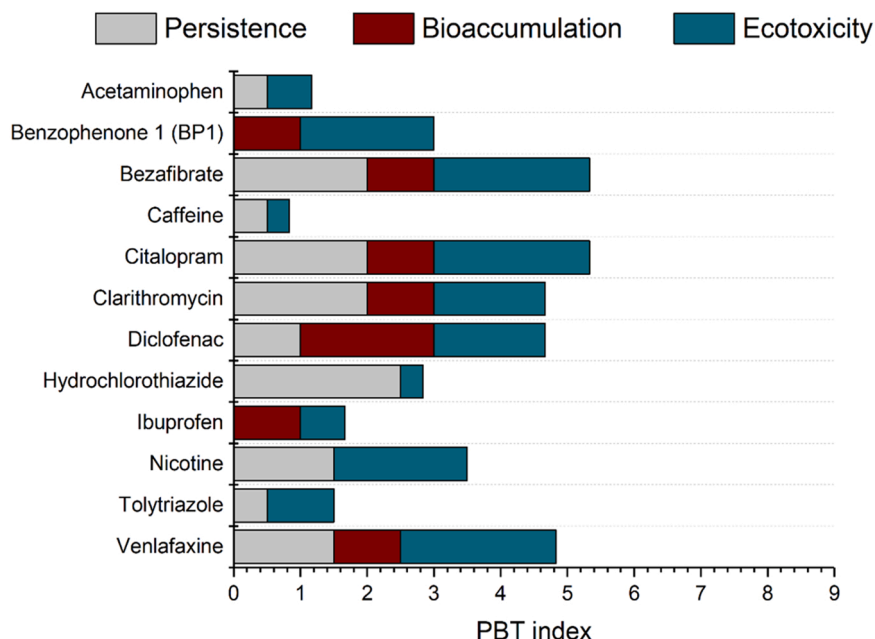
Fig. 6. Hazard assessment of the investigated compounds according to the calculated PBT index and contribution of the inherent compound persistence, bioaccumulation, and toxicity to the total PBT score.

contributors to the relatively high HQ_{sample} values (HQ>0.1) were venlafaxine in all seawater samples (with contribution values between 55% and 75%) and in sample 5_D (81%), benzophenone-1 in sample 8_D (76%), and clarithromycin in samples 30_B (51%) and 31_B (96%) (Fig. S5). This is in line with the conclusions drawn from the individual HQ values.

A PBT index was calculated to assess the inherent capacity of the investigated organic CECs to harm the environment. Results are summarized in Fig. 5. The highest PBT index values were obtained for bezafibrate (5.3), citalopram (5.3), diclofenac (4.7), clarithromycin (4.7), and venlafaxine (4.8). In the case of bezafibrate, citalopram, and clarithromycin, both persistence and toxicity contribute similarly and twice more than bioaccumulation to the total PBT score, whereas the main hazard criteria that contribute to the total PBT score are toxicity in the case of venlafaxine, and bioaccumulation and toxicity in the case of diclofenac. Diclofenac is indeed the compound with the highest bioaccumulation potential of all the chemicals targeted in this study (B score = 2). Therefore, diclofenac analysis in Antarctic biota samples is recommended because relevant levels have been reported to be discharged into the aquatic environment via wastewater [24,46]. Although a recent wide-scope screening conducted in Antarctic phytoplankton samples did not include diclofenac among the anti-inflammatory drugs detected in the cells analyzed [15], this drug has been reported to bioconcentrate in bivalves in mesocosm studies [13] and in bile fish [6]. The lowest PBT index values were obtained for acetaminophen (1.2) and caffeine (0.8). In both cases, persistence is the major contributor to the total PBT score. According to their PBT potential (PBT index above 3) and environmental occurrence in this study (frequency of detection above 30%), citalopram, clarithromycin, nicotine, and venlafaxine can be considered the substances of highest concern in the aquatic environment of the investigated area from the Antarctic Peninsula. Hydrochlorothiazide, with a PBT final score of 2.8 and a detection frequency of 50%, could also be considered of concern, because it is suspected to be highly persistent (P score = 2.5). In this regard, highly persistent chemicals, if continuously released into the environment, could be expected to lead to adverse effects irrespective of their physical-chemical properties [12]. Moreover, highly persistent chemicals can be transported over a greater distance by wind and marine currents and hence, their ubiquitous distribution is foreseen.

4. Conclusions

This work confirms that human activities in Antarctica are responsible for the dispersion of CECs in this continent, leaving a chemical footprint even in areas where research and tourism activities are not concentrated. CEC contamination is not linked strictly to in situ anthropogenic sources. Additional factors such as the higher persistence of organic CECs due to climate conditions in such a high latitude, reemission from ice, or atmospheric deposition (including from marine aerosols) may play a relevant role in the spatial distribution of CEC contamination. A preliminary assessment of the potential ecotoxicological risk that the CEC concentrations measured may pose to exposed organisms suggests low or a moderate risk. However, it is important to highlight that the risk assessment approach used is only focused on twelve CECs and does not consider other CECs (e.g., PFASs and other pharmaceuticals and industrial chemicals) and POPs that surely are present in the aquatic environment of Antarctica. Moreover, the additive model used considers that all CECs have an equal mode of action and neglects synergistic and antagonistic toxicity effects that may occur in the CEC mixture. Wide-scope monitoring of CECs should be conducted in the different environmental compartments, including biota, to elucidate the environmental fate of these contaminants and their effects on the fragile Antarctic terrestrial and marine ecosystems, and identify the CECs of concern in this region that may be overlooked with target methods.

This study also provides evidence of the fact that current measures taken by the existing regulations to protect the pristine environment of Antarctica from human activities are not effective to avoid CEC spread in its aquatic environment. It is urgent to further investigate CEC distribution in Antarctica to draw up a list of substances whose use in this region should be limited or even banned, especially those substances that may pose the greatest environmental risk. Moreover, an effort should be made to implement efficient wastewater treatment systems in all stations to reduce CEC emissions, since wastewater discharges are pointed out as their most relevant source. Additional awareness should be raised among the visitors to reduce the use of these substances.

Environmental implications

The occurrence of organic contaminants of emerging concern in polar remote areas and the associated impact to exposed aquatic organisms has been scarcely investigated, and thus, the submitted manuscript aims at generating new knowledge in this field. To the author`s knowledge, this is the most comprehensive study conducted to date, in terms of the number of inland freshwater samples collected and the extension of the area investigated (previous studies were focused on wastewater and coastal water of Antarctica and/or few freshwater samples (<10). Furthermore, a PBT index is proposed for risk assessment to rank chemicals according to their persistency, bioaccumulation, and toxicity properties.

CRediT authorship contribution statement

Cristina Postigo – formal analysis, visualization, writing – original draft, review & editing. Luis Moreno-Merino – sampling, investigation, conceptualization, writing – review & editing. Ester López-García – investigation. Jerónimo López Martínez –funding acquisition, resources, supervision, writing – review & editing. Miren López de Alda – Conceptualization, funding acquisition, resources, supervision, 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 the work reported in this paper.

Data Availability

Data are stored in github.com and we provide the link in the manuscript.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.131394.

References

[1] Alfaro Garcia, L.A., Descamps, S., Herzke, D., Chastel, O., Carravieri, A., Cherel, Y., et al., 2022. Bioaccumulation of per and polyfluoroalkyl substances in antarctic breeding south polar skuas (Catharacta maccormicki) and their prey. Front Mar Sci 9. ⟨https://www.frontiersin.org/articles/10.3389/fmars.2022.819525⟩.

[2] Aznar-Alemany, Ò., Yang, X., Alonso, M.B., Costa, E.S., Torres, J.P.M., Malm, O., et al., 2019. Preliminary study of long-range transport of halogenated flame retardants using Antarctic marine mammals. Sci Total Environ 650, 1889–1897. https://doi.org/10.1016/j.scitotenv.2018.09.287.

[3] Benfenati E., Cappelli C.I., Petoumenou M.I., Pizzo F., Lomardo A., Albanese F., et al. (2016) PROMETHEUS – Prioritization Of chemicals: a METHodology Embracing PBT parameters into a Unified Strategy. Umweltbundesamt, Dessau-Roßlau. https://www.umweltbundesamt.de/sites/default/files/medien/378/ publikationen/texte_28_2016_prometheus.pdf.

[4] Bhardwaj, L., Chauhan, A., Ranjan, A., Jindal, T., 2018. Persistent organic pollutants in biotic and abiotic components of antarctic pristine environment. Earth Syst Environ 2 (1), 35–54. https://doi.org/10.1007/s41748-017-0032-8.

[5] Boonstra, W.J., Österblom, H., 2014. A chain of fools: or, why it is so hard to stop overfishing. Marit Stud 13 (1), 15. https://doi.org/10.1186/s40152-014-0015-4.

[6] Brozinski, J.-M., Lahti, M., Meierjohann, A., Oikari, A., Kronberg, L., 2013. The anti-inflammatory drugs diclofenac, naproxen and ibuprofen are found in the bile of wild fish caught downstream of a wastewater treatment plant. Environ Sci Technol 47 (1), 342–348. https://doi.org/10.1021/es303031j.

[7] Buerge, I.J., Kahle, M., Buser, H.-R., Müller, M.D., Poiger, T., 2008. Nicotine derivatives in wastewater and surface waters: application as chemical markers for domestic wastewater. Environ Sci Technol 42 (17), 6354–6360. https://doi.org/ 10.1021/es800455q.

[8] Buerge, I.J., Poiger, T., Müller, M.D., Buser, H.-R., 2003. Caffeine, an anthropogenic marker for wastewater contamination of surface waters. Environ Sci Technol 37 (4), 691–700. https://doi.org/10.1021/es020125z.

[9] ChemAxon. (2022). *Marvin version 21.17.0.* ⟨http://www.chemaxon.com/pr oducts/marvin/marvinsketch/⟩.

[10] Cincinelli, A., Scopetani, C., Chelazzi, D., Lombardini, E., Martellini, T., Katsoyiannis, A., et al., 2017. Microplastic in the surface waters of the Ross Sea (Antarctica): Occurrence, distribution and characterization by FTIR. Chemosphere 175, 391–400. https://doi.org/10.1016/j.chemosphere.2017.02.024.

[11] Council of Managers of National Antarctic Programs (COMNAP). (2020). COMNAP Antarctic Facilities.https://github.com/PolarGeospatialCenter/comnap-antarctic-facilities.

[12] Cousins, I.T., Ng, C.A., Wang, Z., Scheringer, M., 2019. Why is high persistence alone a major cause of concern. Environ Sci: Process Impacts 21 (5), 781–792. https://doi.org/10.1039/C8EM00515J.

[13] Daniele, G., Fieu, M., Joachim, S., James-Casas, A., Andres, S., Baudoin, P., et al., 2016. Development of a multi-residue analysis of diclofenac and some transformation products in bivalves using QuEChERS extraction and liquid chromatography-tandem mass spectrometry. Application to samples from mesocosm studies. Talanta 155, 1–7. https://doi.org/10.1016/j. talanta.2016.04.016.

[14] Domínguez-Morueco, N., Moreno-Merino, L., Molins-Delgado, D., Díaz-Cruz, M.S., Aznar-Alemany, Ò., Eljarrat, E., et al., 2021. Anthropogenic contaminants in freshwater from the northern Antarctic Peninsula region. Ambio 50 (3), 544–559. https://doi.org/10.1007/s13280-020-01404-x.

[15] Duarte, B., Gameiro, C., Matos, A.R., Figueiredo, A., Silva, M.S., Cordeiro, C., et al., 2021. First screening of biocides, persistent organic pollutants, pharmaceutical and personal care products in Antarctic phytoplankton from Deception Island by FT-ICR-MS. Chemosphere 274, 129860. https://doi.org/10.1016/j. chemosphere.2021.129860.

[16] Duffy, G.A., Coetzee, B.W.T., Latombe, G., Akerman, A.H., McGeoch, M.A., Chown, S.L., 2017. Barriers to globally invasive species are weakening across the Antarctic. Divers Distrib 23 (9), 982–996. https://doi.org/10.1111/ddi.12593.

[17] European Commission. (1998). Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Communities, L330/32.

[18] European Chemicals Agency (ECHA). (2022). *Information on chemicals.* ⟨https:// echa.europa.eu/information-on-chemicals⟩.

[19] Emnet, P., Gaw, S., Northcott, G., Storey, B., Graham, L., 2015. Personal care products and steroid hormones in the Antarctic coastal environment associated with two Antarctic research stations, McMurdo Station and Scott Base. Environ Res 136, 331–342. https://doi.org/10.1016/j.envres.2014.10.019.

[20] Esteban, S., Moreno-Merino, L., Matellanes, R., Catalá, M., Gorga, M., Petrovic, M., et al., 2016. Presence of endocrine disruptors in freshwater in the northern Antarctic Peninsula region. Environ Res 147, 179–192. https://doi.org/10.1016/j. envres.2016.01.034.

[21] European Commission. (2003). Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Part II: Environmental Risk Assessment. ⟨https://echa.europa.eu/documents/10162/ 987906/tgdpart2_2ed_en.pdf/138b7b71-a069–428e-9036–62f4300b752f⟩.

[22] Fromant, A., Carravieri, A., Bustamante, P., Labadie, P., Budzinski, H., Peluhet, L., et al., 2016. Wide range of metallic and organic contaminants in various tissues of the Antarctic prion, a planktonophagous seabird from the Southern Ocean. Sci Total Environ 544, 754–764. https://doi.org/10.1016/j.scitotenv.2015.11.114.

[23] Gao, H., Na, G., Yao, Y., Li, R., Gao, Y., Zhang, Z., et al., 2018. Distribution characteristics and source of dechloranes in soil and lichen of the fildes peninsula (Antarctica. Int J Environ Res Public Health 15 (Issue 10). https://doi.org/ 10.3390/ijerph15102312.

[24] González-Alonso, S., Merino, L.M., Esteban, S., López de Alda, M., Barceló, D., Durán, J.J., et al., 2017. Occurrence of pharmaceutical, recreational and psychotropic drug residues in surface water on the northern Antarctic Peninsula region. Environ Pollut 229, 241–254. https://doi.org/10.1016/j. envpol.2017.05.060.

[25] González-Pleiter, M., Edo, C., Velázquez, D., Casero-Chamorro, M.C., Leganés, F., Quesada, A., et al., 2020. First detection of microplastics in the freshwater of an Antarctic Specially Protected Area. Mar Pollut Bull 161, 111811. https://doi.org/ 10.1016/j.marpolbul.2020.111811.

[26] Hernández, F., Calisto-Ulloa, N., Gómez-Fuentes, C., Gómez, M., Ferrer, J., González-Rocha, G., et al., 2019. Occurrence of antibiotics and bacterial resistance

in wastewater and sea water from the Antarctic. J Hazard Mater 363, 447–456. https://doi.org/10.1016/j.jhazmat.2018.07.027.

[27] Houde, M., De Silva, A.O., Muir, D.C.G., Letcher, R.J., 2011. Monitoring of perfluorinated compounds in aquatic biota: an updated review. Environ Sci Technol 45 (19), 7962–7973. https://doi.org/10.1021/es104326w.

[28] International Association of Antarctica Tour Operators (IAATO). (2020). IAATO Antarctic visitor figures 2019/2020. https://iaato.org/wp-content/uploads/2020/06/IAATO-on-Antarctic-visitor-figures-2019-20-FINAL.pdf.

[29] Kallenborn, R., Hung, H., Brorström-Lundén, E., 2015. Chapter 13 - atmospheric long-range transport of persistent organic pollutants (POPs) into Polar Regions. In: Zeng, E.Y. (Ed.), Comprehensive Analytical Chemistry, 67. Elsevier, pp. 411–432. https://doi.org/10.1016/B978-0-444-63299-9.00013-2.

[30] Khairy, M., Brault, E., Dickhut, R., Harding, K.C., Harkonen, T., Karlsson, O., et al., 2021. Bioaccumulation of PCBs, OCPs and PBDEs in marine mammals from west antarctica. Front Mar Sci 8. ⟨https://www.frontiersin.org/articles/10.3389/fmars.2021.768715⟩.

[31] Kuepper, N.D., Böhm, L., Braun, C., Bustamante, P., Düring, R.-A., Libertelli, M.M., et al., 2022. Persistent organic pollutants and mercury in a colony of Antarctic seabirds: higher concentrations in 1998, 2001, and 2003 compared to 2014 to 2016. Polar Biol 45 (7), 1229–1245. https://doi.org/10.1007/s00300-022-03065-w.

[32] Legrand, M., Preunkert, S., Jourdain, B., Guilhermet, J., Fa{ï}n, X., Alekhina, I., et al., 2013. Water-soluble organic carbon in snow and ice deposited at Alpine, Greenland, and Antarctic sites: a critical review of available data and their atmospheric relevance. Climate 9 (5), 2195–2211. https://doi.org/10.5194/cp-9-2195-2013.

[33] Lewis, P.J., Lashko, A., Chiaradia, A., Allinson, G., Shimeta, J., Emmerson, L., 2022. New and legacy persistent organic pollutants (POPs) in breeding seabirds from the East Antarctic. Environ Pollut 309, 119734. https://doi.org/10.1016/j.envpol.2022.119734.

[34] Martin, T. (2016). *Toxicity Estimation Software Tool (TEST)*. U.S. Environmental Protection Agency, Washington, DC. ⟨https://www.epa.gov/chemical-research/toxicity-estimation-software-tool-test⟩.

[35] Morales, P., Roscales, J.L., Muñoz-Arnanz, J., Barbosa, A., Jiménez, B., 2022. Evaluation of PCDD/Fs, PCBs and PBDEs in two penguin species from Antarctica. Chemosphere 286, 131871. https://doi.org/10.1016/j.chemosphere.2021.131871.

[36] Moreno, L., Silva-Busso, A., López-Martínez, J., Durán-Valsero, J.J., Martínez-Navarrete, C., Cuchí, J.A., et al., 2012. Hydrogeochemical characteristics at Cape Lamb, Vega Island, Antarctic Peninsula. Antarct Sci 24 (6), 591–607 https://doi.org/DOI: 10.1017/S0954102012000478.

[37] Network of refernce laboratories, research centres and related organisations for monitoring of emerging environmental substances (NORMAN). (2022). *NORMAN Ecotoxicology Database*. ⟨https://www.norman-network.com/nds/ecotox/⟩.

[38] Olalla, A., Moreno, L., Valcárcel, Y., 2020. Prioritisation of emerging contaminants in the northern Antarctic Peninsula based on their environmental risk. Sci Total Environ 742, 140417. https://doi.org/10.1016/j.scitotenv.2020.140417.

[39] Olker, J.H., Elonen, C.M., Pilli, A., Anderson, A., Kinziger, B., Erickson, S., et al., 2022. The ecotoxicology knowledgebase: a curated database of ecologically relevant toxicity tests to support environmental research and risk assessment. Environ Toxicol Chem 41 (6), 1520–1539. https://doi.org/10.1002/etc.5324.

[40] Panti, C., Muñoz-Arnanz, J., Marsili, L., Panigada, S., Baini, M., Jiménez, B., et al., 2022. Ecotoxicological characterization of type C killer whales from terra nova bay (ross sea, antarctica): molecular biomarkers, legacy, and emerging persistent organic contaminants. Front Mar Sci 9. ⟨https://www.frontiersin.org/article/10.3389/fmars.2022.818370⟩.

[41] Ríos, J.M., Mammana, S.B., Moreira, E., Poma, G., Malarvannan, G., Barrera-Oro, E., et al., 2021. Accumulation of PBDEs and MeO-PBDEs in notothenioid fish from the South Shetland Islands, Antarctica: An interspecies comparative study. Mar Pollut Bull 168, 112453. https://doi.org/10.1016/j.marpolbul.2021.112453.

[42] Schiavone, A., Corsolini, S., Borghesi, N., Focardi, S., 2009. Contamination profiles of selected PCB congeners, chlorinated pesticides, PCDD/Fs in Antarctic fur seal pups and penguin eggs. Chemosphere 76 (2), 264–269. https://doi.org/10.1016/j.chemosphere.2009.03.007.

[43] Secretariat of the Antarctic Treaty, 1991. The Protocol on Environmental Protection to the Antarctic Treaty. Madrid. ⟨https://www.ats.aq/e/protocol.html⟩.

[44] sen Gupta, R., Sarkar, A., Kureishey, T.W., 1996. PCBs and organochlorine pesticides in krill, birds and water from Antartica. Deep Sea Res Part II Top Stud Oceanogr 43 (1), 119–126. https://doi.org/10.1016/0967-0645(95)00086-0.

[45] Sladen, W.J.L., Menzie, C.M., Reichel, W.L., 1966. DDT residues in adelie penguins and a crabeater seal from antarctica. Nature 210 (5037), 670–673. https://doi.org/10.1038/210670a0.

[46] Szopińska, M., Potapowicz, J., Jankowska, K., Luczkiewicz, A., Svahn, O., Björklund, E., et al., 2022. Pharmaceuticals and other contaminants of emerging concern in Admiralty Bay as a result of untreated wastewater discharge: Status and possible environmental consequences. Sci Total Environ 835, 155400. https://doi.org/10.1016/j.scitotenv.2022.155400.

[47] Trumble, S.J., Robinson, E.M., Noren, S.R., Usenko, S., Davis, J., Kanatous, S.B., 2012. Assessment of legacy and emerging persistent organic pollutants in Weddell seal tissue (Leptonychotes weddellii) near McMurdo Sound, Antarctica. Sci Total Environ 439, 275–283. https://doi.org/10.1016/j.scitotenv.2012.09.018.

[48] US Environmental Protection Agency (EPA). (2022). *Estimation Programs Interface Suite^{TM} for Microsoft® Windows, v 4.11*. United States Environmental Protection Agency, Washington, DC, USA. ⟨https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface⟩.

[49] Vecchiato, M., Gregoris, E., Barbaro, E., Barbante, C., Piazza, R., Gambaro, A., 2017. Fragrances in the seawater of Terra Nova Bay, Antarctica. Sci Total Environ 593–594, 375–379. https://doi.org/10.1016/j.scitotenv.2017.03.197.

[50] Wang, D., Ma, H., Chen, Z., Shi, G., 2022. Occurrences and possible sources of persistent organic pollutants (POPs) in ice-free area soils in East Antarctica. CATENA 212, 106083. https://doi.org/10.1016/j.catena.2022.106083.

[51] Wennmalm, Å., Gunnarsson, B., 2005. Public health care management of water pollution with pharmaceuticals: environmental classification and analysis of pharmaceutical residues in sewage water. Drug Inf J 39 (3), 291–297. https://doi.org/10.1177/009286150503900307.

[52] Williams, A.J., Grulke, C.M., Edwards, J., McEachran, A.D., Mansouri, K., Baker, N.C., et al., 2017. The CompTox Chemistry Dashboard: a community data resource for environmental chemistry. J Chemin- 9 (1), 61. https://doi.org/10.1186/s13321-017-0247-6.

[53] Xie, J., Tao, L., Wu, Q., Bian, Z., Wang, M., Li, Y., et al., 2022. Bioaccumulation of organochlorine pesticides in Antarctic krill (Euphausia superba): Profile, influencing factors, and mechanisms. J Hazard Mater 426, 128115. https://doi.org/10.1016/j.jhazmat.2021.128115.

[54] Xie, Z., Wang, Z., Magand, O., Thollot, A., Ebinghaus, R., Mi, W., et al., 2020. Occurrence of legacy and emerging organic contaminants in snow at Dome C in the Antarctic. Sci Total Environ 741, 140200. https://doi.org/10.1016/j.scitotenv.2020.140200.

[55] Xie, Z., Zhang, P., Wu, Z., Zhang, S., Wei, L., Mi, L., et al., 2022. Legacy and emerging organic contaminants in the polar regions. Sci Total Environ 835, 155376. https://doi.org/10.1016/j.scitotenv.2022.155376.