



## Pharmaceuticals and other contaminants of emerging concern in Admiralty Bay as a result of untreated wastewater discharge: Status and possible environmental consequences



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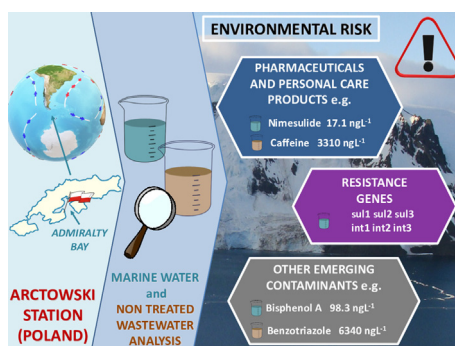
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### HIGHLIGHTS

- Anthropogenic activity has an impact on Antarctic ecosystems.
- Emerging contaminants are emitted via non-treated wastewater discharge.
- Study shows ketoconazole, diclofenac, ibuprofen and caffeine pose the greatest risk.
- Antibiotic resistance genes and integrons were present in the studied samples.
- A general strategy for reducing emissions of emerging contaminants is needed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Considering how the impact of human activity in Antarctica is growing, the aim of this study was to conduct the first assessment of pharmaceuticals and personal care products (PPCPs), other emerging contaminants (ECs), and antibiotic resistance genes present in the western shore of the Admiralty Bay region of King George Island. In total, more than 170 substances were evaluated to assess the potential environmental risks they pose to the study area. The major evaluated source of pollutants in this study is discharged untreated wastewater. The highest PPCP concentrations in wastewater were found for naproxen (2653 ngL<sup>-1</sup>), diclofenac (747 ngL<sup>-1</sup>), ketoconazole (760 ngL<sup>-1</sup>), ibuprofen (477 ngL<sup>-1</sup>) and acetaminophen (332 ngL<sup>-1</sup>). Moreover, the concentrations of benzotriazole (6340 ngL<sup>-1</sup>) and caffeine (3310 ngL<sup>-1</sup>) were also high. The Risk Quotient values indicate that azole antifungals (ketoconazole), anti-inflammatories (diclofenac, ibuprofen) and stimulants (caffeine) are the main groups responsible for the highest toxic burden. In addition, antibiotic resistance genes integrons (int 1) and sulphonamide resistance genes (sul 1–2) were detected in wastewater and seawater. These results indicate that regular monitoring of PPCPs and other ECs is of great importance in this environment. Additionally, the following mitigation strategies are suggested: (1) to create a centralised record of the medications prescribed and consumed in situ (to improve knowledge of potential contaminants without analysis); (2) to use more environmentally friendly substitutes both for pharmaceuticals and personal care products when possible (limiting consumption at the source); and (3) to apply advanced systems for wastewater treatment before discharge to the recipient (end-of-pipe technologies as a final barrier).

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## 1. Introduction

Today, human activity is having an ever-growing impact on the environment, while there is also increasing interest in nature preservation. Consequently, a detailed characterisation of emerging contaminants (ECs) in the aquatic environment is of primary importance. In the Antarctic ecosystem, where very little information is available even today (Smith and Riddle, 2009), holistic approaches and actions to prevent, remedy, restore, and monitor the pollution of water is needed. The concepts for a *Water-Smart Society* in Europe means that the value of water is appreciated and all water sources are properly managed, e.g., water scarcity and pollution of water are avoided and closed water loops are implemented (Water Europe, The value of water). These concepts, however, are supposed to be considered not only in Europe but worldwide to foster a circular economy and optimal water resource efficiency. Under such conditions the water system will also be resilient against the impact of climate change events (Water Europe, 2021). Overall, this describes the *Zero Pollution Action Plan* and fits within the *European Green Deal* objectives, which also might be applied to polar regions, where proper wastewater management is still under evaluation (Water Europe, 2021). Wastewater treatment and disposal is a challenge for all countries managing Antarctic research stations, as they may pose a threat to the environment and to human health in the Antarctic Region (Connor, 2008; Gröndahl et al., 2009). There is a total of 82 summer and all-year-round research stations in the Antarctic (COMNAP, 2013). Most of the stations are located along the coasts, and they discharge treated and untreated wastewater directly into the marine environment (Hughes, 2004). Stations that are remote from the seashore use deep ice pits or subsurface ice wells (Stark et al., 2015). Due to the environmental conditions, the harsh Antarctic climate and the properties of the wastewater, the use of effective wastewater treatment technologies is a challenge for all research station infrastructures. The weak point of the wastewater management strategy is that since 2009 there has been no open-access report available regarding the current situation in Antarctica. Recent data shows that of the 44 all-year-round stations, 37% do not have any type of wastewater treatment, while as many as 69% of summer stations lack treatment (Gröndahl et al., 2009; Hughes, 2004).

The main document describing proper waste management in Antarctica is the *Protocol on Environmental Protection to the Antarctic Treaty* (Protocol), primarily Annex III, Waste Disposal and Waste Management. The annex obliges the countries managing research stations to reduce wastewater (both production and disposal) as much as possible in order to minimise impact on the environment. The Protocol was adopted in 1991 and, since then, our knowledge regarding the environmental threat of a wide range of contaminants has increased significantly (Bouissou-Schurtz et al., 2014; Minguez et al., 2016; Straub and Stewart, 2007). The Protocol allows for the discharge of sewage and domestic liquid waste directly into the sea (Annex III, Article 5), but only where the discharge takes place into an environment that allows dilution and rapid dispersion. When the number of inhabitants in a research station, e.g., during the summer period, is 30 or more, the sewage must be treated at least by maceration before discharging it into the sea (Stark et al., 2015). But dilution is not a proper solution for ECs (including PPCPs). Some scientific Antarctic stations use much stricter standards (based on their national requirements) than required by the Protocol. For example, the wastewater treatment plant (WWTP) installed in New Zealand's Scott Base in 2001/02 was designed to meet the national standards then in force in New Zealand (Connor, 2008). Despite restrictive regulations and effective methods of wastewater management at research stations in Antarctica, the presence of long-lasting emerging contaminants (ECs) in the environment, e.g., pharmaceuticals and personal care products (PPCPs) detergents and even microplastics, is worrying (Bhardwaj et al., 2018).

The concentrations of PPCPs and illicit drugs in Antarctica has been quite little studied (Emnet et al., 2015; Esteban et al., 2016; González-Alonso et al., 2017). After human consumption, pharmaceuticals are known to be excreted – via urine and feces – as the parent compound

and/or metabolites thereof. Personal care products are primarily intended for external use on the human body and therefore undergo few metabolic changes (Ternes et al., 2004). Overall, there is a risk of PPCP emission to the Antarctic environment through the discharge of both treated and untreated wastewater. Under natural conditions, PPCPs might be degraded via photodegradation, hydrolysis and microbial degradation processes (Caliman and Gavrilescu, 2009). However, because of the simultaneous presence of many types of PPCPs and other emerging contaminants (EC) and their regular release, a relatively high level of persistence in the environment is afforded to many of these chemicals (Daughton and Ternes, 1999; Muñoz et al., 2008). The harsh Antarctic climate, characterised by low temperatures, polar night periods, and the presence of ice in the coastal seawater zone, may contribute to a decreased degradation of PPCPs, which will result in their prolonged persistence in the environment (Emnet et al., 2015). Antibiotics disseminated with wastewater may also favour the selection of resistant populations naturally occurring in the microbiota of the receiving waters (Martínez, 2012). This is of serious concern in the pristine Antarctic environment, as it leads to changes in the original resistome and to genetic homogenisation of the bacterial community (Cowan et al., 2011; Rabbia et al., 2016). Additionally, the discharge of wastewater may enrich the environment with mobile genetic elements, such as conjugative plasmids, transposons and integrons (Kotlarska et al., 2015; Marano and Cytryn, 2018), which act as effective carriers of antibiotic resistance genes (ARGs).

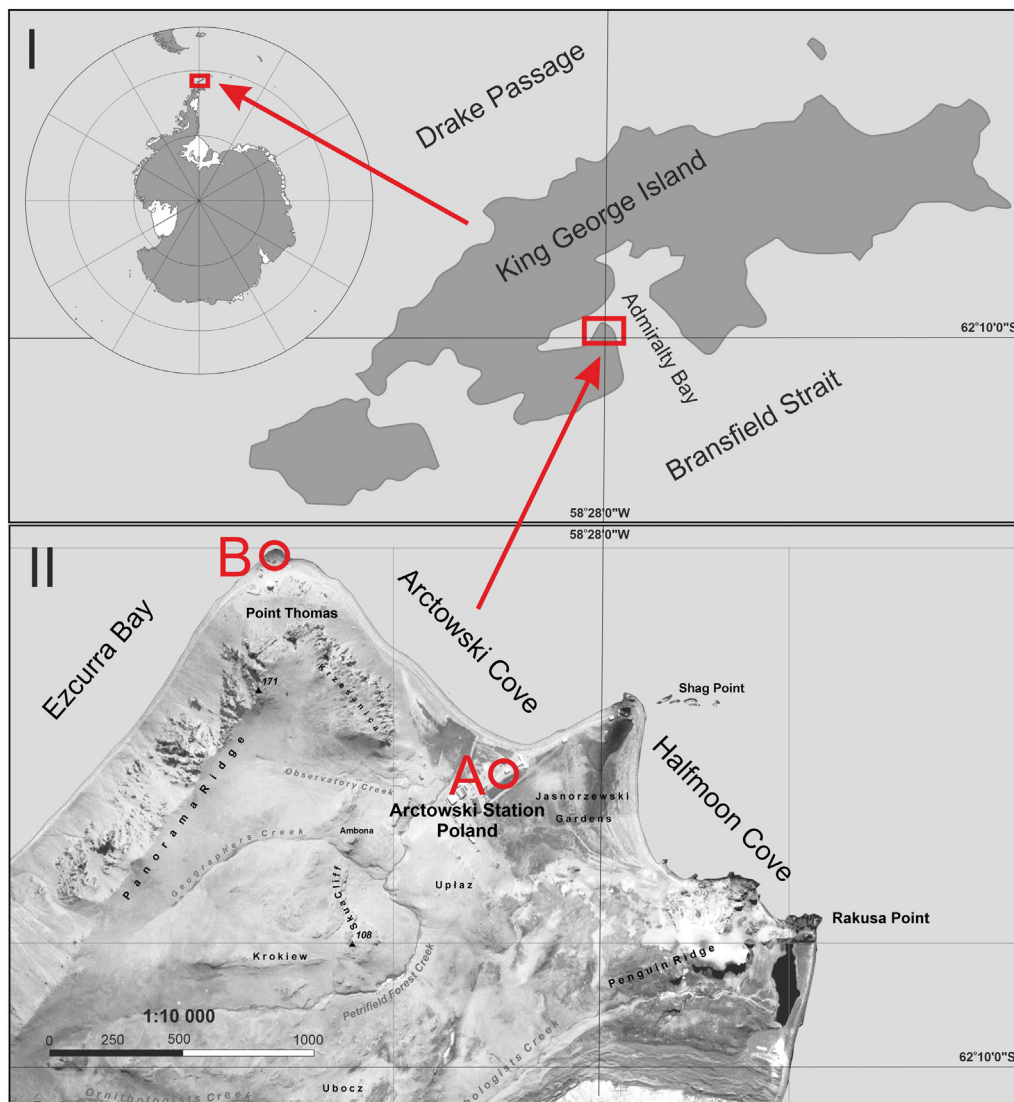
An investigation on the presence of organic matter, trace metals (Pb, Fe, Cd, Zn, Cu, Ni, Co, and Cr), different groups of surfactants (non-ionic, cationic and anionic) and formaldehyde concentration in the samples of wastewater and sweater (its recipient) examined both in 2017 and 2019 is summarised in (Szopińska et al., 2021). The aim of this work was to assess the occurrence of emerging contaminants (pharmaceutical and personal care products, illegal drugs and a few industrial chemicals) as well as selected antibiotic-resistance genes and integrons in wastewater and its receiver in the western shore of Admiralty Bay (King George Island). This is the first such study ever conducted in this region. Hence, the main objectives were: (I) to determine the presence of a wide range organic micropollutants; (II) to characterise ARGs (III) to estimate the environmental risk that the detected substances and genes pose to aquatic Antarctic ecosystems; and (IV) to propose prevention and mitigation solutions to minimise their negative impacts.

## 2. Materials and methods

### 2.1. Study area and sampling design

The study area was the western shore of Admiralty Bay in the vicinity of Arctowski Station (Poland), King George Island, South Shetland Islands, Antarctic Peninsula, as shown in Fig. 1. It is a small, ice-free area characterised by a cold, maritime climate (Falk et al., 2018; Vaughan et al., 2003). Long-term climatic observations in the Arctowski Station for the years 1977–98 provided the basis for the calculation of the mean annual air temperature of  $-1.6\text{ }^{\circ}\text{C}$  and total annual precipitation of 499.8 mm (Marsz, 2000).

The Arctowski Station consists of fifteen separate buildings and does not have a WWTP unit. The station has four buried septic tanks to which sewage (grey and black water) is fed from individual facilities. Details on each of the tanks and water consumption at the station are described elsewhere (Szopińska et al., 2021). Drinking and hygiene water is provided from the lake next to the station buildings. The lake is fed by the Petrified Forest Creek, which has its source at the Warszawa Icefield glacier's front. The maximum number of inhabitants at the station during the peak of the summer season can reach 37, while in the winter season, the staff consists of only eight people, who are responsible for station maintenance and long-term monitoring programmes. Daily water consumption at the Arctowski Station in 2016–19 was on average about 149 L per person per day, while it is estimated that the total annual amount of sewage produced is from 31.4 to 80.7 m<sup>3</sup> (Szopińska et al., 2021).



**Fig. 1.** Location of sampling points: (I) in the context of Antarctic continent and (II) considering their geographic location at the western shore of Admiralty Bay (Arctowski Station, King George Island) presented in a fragment of the orthophotomap by Pudelko (2007).

Wastewater samples were taken from the tank near the main building (Fig. 1, sampling point A) where non-solid waste is macerated. This tank is connected to the main building and the laboratory. The liquid residues of the septic tanks are discharged into Admiralty Bay (Fig. 1, sampling point B) at the entrance to Ezcurra Bay at the foot of Point Thomas hill. Transport is organised periodically (depending on the number of people accommodated at the station) via sewage tanker. As part of this study, wastewater and seawater samples were collected during two polar expeditions carried out on January 18–20, 2017 and April 1–5, 2019. To evaluate the degree of wastewater dispersion, seawater samples at point 2 were collected: (1) before and (2) directly after discharge (at 0 h), and (3) after 2 h and 24 h in 2017 and after 1 h, 2 h, 24 h, 48 h and 96 h in 2019. The samples were taken manually into 1-L polyethylene containers. Each bottle was rinsed three times with the sampled water at the collection site. Then, the sewage and water samples were stored at  $-20\text{ }^{\circ}\text{C}$  until sample preparation, which was conducted just prior to analysis.

## 2.2. Chemicals and reagents

For the applied analytical methods, mobile phase chemicals, including acetonitrile (ACN) and methanol (MeOH), were HPLC-grade (Svahn and Björklund, 2016) and LC-MS grade (Ofrydopoulou et al., 2021), and were

purchased from Fisher Scientific (Gothenburg, Sweden), Sigma-Aldrich (Steinheim, Germany) and Merck KGaA (Darmstadt, Germany). Formic acid (FoA), ammonium hydroxide solution (25% sol.), ammonium hydrogen carbonate, disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{EDTA}$ ), ascorbic acid and ammonium hydroxide were purchased from Sigma-Aldrich (Steinheim, Germany) and Merck KGaA (Darmstadt, Germany).

All reference standards for PPCPs were of high purity grade (>98%) and supplied by Promochem (Wesel, Germany), Fluka and Sigma-Aldrich (Steinheim, Germany) and from Sigma-Aldrich Sweden AB (Stockholm, Sweden). Illicit drugs were kindly donated by the Forensic Medical School of the Aristotle University of Thessaloniki. Stock standard solutions ( $1000\text{ mg}\cdot\text{L}^{-1}$ ) were prepared in methanol (LC-MS grade) and stored in darkness at  $-20\text{ }^{\circ}\text{C}$ . Working solutions were prepared in methanol/water 50/50 (v/v) and their stability was checked on a trimestral basis.

Oasis HLB cartridges ( $200\text{ mg}$ ,  $6\text{ cm}^3$ ) were purchased from Waters Corporation (Milford, MA, U.S.A.).

## 2.3. Analytical methods for PPCPs and other ECs

All samples (seawater and wastewater) collected in 2017 and 2019 were tested for PPCPs and other ECs (analysis of whole water together with suspended solids) in accordance with previously developed protocols



(Svahn and Björklund, 2016, 2019). In 2019, the chemical analysis was expanded and samples were analysed for a wider range of PPCPs and illicit drugs using an optimised multiresidue method (Ofrydopoulou et al., 2021), enabling screening for 172 ECs in the dissolved phase. The main steps of both methodologies are presented in the following subsection.

### 2.3.1. Sample preparation

Upon collection, the water samples were transported in portable freezers and thereafter stored in a freezer at  $-20\text{ }^{\circ}\text{C}$ . Prior to sample preparation, the samples were left out to reach room temperature.

Whole sample analysis (including of solid parts) was performed according to the following protocol. Wastewater samples (50 g each) were loaded on SPE cartridges (Oasis HLB 200 mg,  $6\text{ cm}^3$ ) manually packed with 2 g finely ground sand (on top of the HLB material) for pre-filtration using a traditional SPE set-up with negative pressure application. Marine water samples were prepared using high-flow-rate sample loading (500 g each) with the application of positive pressure and finely ground sand (2 g) as an SPE-column in-line filter according to Svahn and Björklund (2019). Next, samples were dried, eluted, reconstituted and analysed by ultra-performance liquid chromatography-electrospray tandem mass spectrometry (UPLC-ESI-MS/MS). A detailed description of method validation parameters and chromatographic conditions are available in (Svahn and Björklund, 2016, 2019).

Selected samples from the 2019 sampling campaign were analysed for a wider range of analytes including pharmaceuticals and illegal drugs in the dissolved phase. Detailed information of the main properties of the target compounds can be found in (Ofrydopoulou et al., 2021, 2022). The dissolved phase of the samples was analysed using the following procedure. Water samples (200 mL for wastewater and 500 mL for water) were filtered (1- $\mu\text{m}$  glass fibre filters GF/B, Whatman, UK) and subjected to solid-phase extraction (SPE) according to a previously published protocol Ofrydopoulou et al. (2021) after some modifications. In brief, the HLB cartridges were conditioned with methanol and water, taking care not to allow the sorbent to dry out prior to loading the sample. Afterwards, the cartridges were washed with water and vacuum dried, and analytes were eluted with methanol. The final eluent was concentrated under a gentle stream of nitrogen nearly to dryness and reconstituted in 1 mL of methanol/water 50:50 (v/v). Prior to analysis, all samples were filtered through PTFE filters (0.22  $\mu\text{m}$ ).

### 2.3.2. Instrumentation and chromatographic analysis

Whole water analysis of PPCP was performed using a Waters Acquity ultra-high-performance liquid chromatography UPLC H-Class, which was equipped with a Quaternary Solvent Manager (QSM), a Sample Manager with Flow-Through Needle (SM-FTN) and a Column Manager (CM) enabling fast column switching (Waters, Milford, MA). A Xevo TQ-STM triple quadrupole mass spectrometer (Waters Micromass, Manchester, UK) equipped with a Z-spray electrospray interface was used.

Moreover, for PPCPs analysis in the dissolved phase of selected samples, an ultra-high-performance liquid chromatography (UHPLC) – high-resolution mass spectrometry (HRMS) system was used. The MS system was a Q Exactive Focus Orbitrap equipped with a heated electrospray ionization source (H-ESI II, Thermo Scientific, Bremen, Germany). The Orbitrap analyser was operated at a resolution of 70,000 for full-scan MS (FS) and 17,500 for data-dependent acquisition (ddMS2). The mass range was set at 100–1000 Da and 50–1000 Da for FS and ddMS2, respectively. Details of the applied chromatographic methodologies are described in (Svahn and Björklund, 2016; Ofrydopoulou et al., 2021).

### 2.3.3. Quality assurance/quality control (QA/QC)

Method performance was based on Environmental Protection Agency Method no. 1694 and the EU regulations (European Commission Decision, 2002) as well as the ISO/IEC 17025:2017 guidelines. In brief, a system suitability solution containing representative analytes was analysed to check system performance. A method blank was analysed to ensure the absence of target analytes, while solvent blanks were analysed within the sequence to check for any potential carry-over effects. A five-point matrix-matched calibration curve was analysed at the beginning and end of the batch. A

quality control (QC) sample was prepared under the same conditions as the samples and injected every twenty samples. For a reliable identification of the target analytes, the following criteria were established: (a) the retention time difference between the standards and the unknowns should be  $\pm 0.1\text{ min}$ , (b) the mass error of the quantification peak should be not more than  $\pm 5\text{ ppm}$ , (c) at least one fragment ion should be present, (d) the isotopic pattern matching should be  $>75\%$ , and (e) the analyte area should be at levels  $>10^4$ . Detailed information on the method performance (dissolved phase analysis) is summarised in Table S1 (Supplementary Material).

### 2.4. Analysis of antibiotic resistance genes and integrons

Samples ( $V = 1\text{ L}$ ) were filtered through polycarbonate membrane filters (0.22  $\mu\text{m}$ ) and stored at  $-20\text{ }^{\circ}\text{C}$  until DNA extraction. DNA was extracted using the Genomic Mini AX Bacteria+ (A&A Biotechnology, Poland) according to the manufacturer's instructions. The DNA concentration was measured using a NanoDrop® Spectrophotometer ND-1000 (Thermo Scientific, Waldham, USA). In this study, the Bacterial 16S rRNA genes, resistance genes *sul 1*, *sul 2* and *sul 3*, together with the class 1 to class 3 integron integrase *int 1*, *int 2* and *int 3* gene were analysed. Sequences of primers were used according to Barraud et al. (2010), Ferris et al. (1996), Pei et al. (2006). qPCR assays were performed with a reaction mixture of 20  $\mu\text{L}$  containing: 10  $\mu\text{L}$  of Real Time 2xRT-PCR Mix SYBR A (A&A Biotechnology), 0.4  $\mu\text{L}$  of respective primers (stock concentration 10  $\mu\text{M}$ ), 1  $\mu\text{L}$  of extracted DNA template (10  $\text{ng}\mu\text{L}^{-1}$ ) and 8.2  $\mu\text{L}$  of nuclease-free water. The qPCR cycling programme consisted of 3 min of initial denaturation at  $95\text{ }^{\circ}\text{C}$ , followed by 40 cycles of: denaturation at  $95\text{ }^{\circ}\text{C}$  for 15 s, followed by primer annealing at  $60\text{ }^{\circ}\text{C}$  for 30 s ( $58\text{ }^{\circ}\text{C}$  for bacterial 16S rRNA genes) and primer elongation at  $72\text{ }^{\circ}\text{C}$  for 30 s. Melting curves were obtained to confirm amplification specificity. Assays were performed in triplicate with a MX3005P real-time detection system (Stratagene® Agilent Technologies). The results were presented as copies of resistance genes normalised to the number of Bacterial 16S rRNA genes, which assess the level of *sul 1–3* and *int 1–3* proportional to the size of the overall population. The standard deviation of six replicates in three independent q-PCR runs was calculated.

### 2.5. Environmental risk assessment data analysis

An ecological risk assessment can be performed to evaluate the potential adverse ecological effects on recipient aquatic ecosystems. Following the recommendations of the European regulatory guidance – the European Technical Guidance Document on Risk Assessment (de Bruijn and ten Heuvelhof, 2002), risk quotients (RQs) were applied to assess the potential aquatic ecological risks of detected and measured concentration of ECs and was calculated by Eq. (1):

$$\text{RQ} = \frac{\text{MEC}}{\text{PNEC}} \quad (1)$$

where MEC is the measured environmental concentration and PNEC the predicted no-effect concentration. The PNEC values for marine organisms were obtained from the NORMAN Ecotoxicology Database [NORMAN], or other literature data sources, if available.

According to the data presented by the NORMAN Ecotoxicology Database, most of the lowest PNEC values were derived for freshwater organisms. An experimental value for marine water organisms was calculated using the following equation:

$$\text{PNEC}_{\text{marine water}} = \frac{\text{Lowest PNEC}_{\text{fresh water}}}{10} \quad (2)$$

## 3. Results and discussion

Recently, scientists underlined the problem of synergistic interactions between growing stressors in the ecosystems of polar regions (Arrigo et al., 2020). Stressors are related to both global climate change and

increased human activity (scientific and touristic). Specifically they may also include overfishing, mining, long range transport of pollution, ineffective wastewater management etc. Not all constitute threat for Antarctic region, however the last will be further discussed in details.

### 3.1. Pharmaceuticals and personal care products, illegal drugs and other ECs

The classification of PPCPs and other ECs detected and determined in the studied samples from the two campaigns in 2017 and 2019 (whole water analysis) is presented in Table 1, dividing the pollutants into different groups. Table 2 summarises the results of the targeted compound determination in 2019 (dissolved phase). The whole database of obtained results on analysed micropollutants under both field campaigns is listed in Supp. Mat. (Table S2–S4). In the individual environmental samples, up to 14.81% of the tested chemicals were detected, although in the least polluted samples, any of compounds from the PPCPs, illegal drugs and ECs groups were detected (Table S5, Supp. Mat.). Moreover, it was found that some groups of impurities were not detected at all (e.g., antineoplastics, urinary tract pharmaceuticals, antipsychotic drugs).

The overall results (Table 1) revealed that among the wide range of ECs analysed, thirteen could be detected and quantified in the wastewater samples. The data represents grab sampling results, and the total emission of ECs might differ each season due to variation in the consumption patterns of visitors. Medicine consumption may differ even among countries (Kaiser et al., 2019). Additionally, the number of station visitors may vary over the year (Besse et al., 2008; Szopińska et al., 2021).

The highest concentrations in wastewater samples were detected for three pharmaceuticals: diclofenac (DIC; 74–747 ngL<sup>-1</sup>), naproxen (NAP; 662–2653 ngL<sup>-1</sup>) and ketoconazole (KCZ; 760 ngL<sup>-1</sup>), as well as for benzotriazole (BTA, 72–6340 ngL<sup>-1</sup>), which is widely used as a corrosion inhibitor (Montesdeoca-Esponda et al., 2019) (Table 1). Moreover, PPCPs such as acetaminophen (APAP) – commonly known as paracetamol – was determined in 2019 (332 ngL<sup>-1</sup>) together with ibuprofen (IBP, 477 ngL<sup>-1</sup>) and caffeine (CAF, 3310 ngL<sup>-1</sup>) (Table 2). Results presented by (González-Alonso et al., 2017) showed that the highest concentrations observed for PPCPs in analysed untreated wastewater in the northern Antarctic Peninsula region were found for the analgesic pharmaceuticals APAP (48.74 µgL<sup>-1</sup>), DIC (15.09 µgL<sup>-1</sup>) and IBP (10.05 µgL<sup>-1</sup>), and for the stimulant CAF (71.33 µgL<sup>-1</sup>). Those samples were taken in 2012/13. Some nonsteroidal anti-inflammatory drugs (NSAIDs, DIC), analgesic-antipyretics (APAP) and central-nervous stimulants (CAF) are common for these two

independent studies. One or more of these three PPCPs might be a good candidate as a marker of anthropogenic pollution for the international monitoring of other scientific stations. CAF, for example, has been suggested as a marker of recent faecal contamination of river water used for drinking water and was detected in more than 90% of the analysed river water samples (Daneshvar et al., 2012). All the above-mentioned compounds are undoubtedly anthropogenic and their emission to the Antarctic environment should be strongly limited in the near future.

DIC belongs to the pharmaceutical of group musculo-skeleton system and is an NSAID. The pharmaco-kinetical excretion rate is up to 15% (Ferrari et al., 2003; Ternes, 1998). Based on our results (Tables 1 and 2) only traces could be detected after wastewater discharge. However, the newest scientific reports underline the need for its removal from wastewater to protect water resources (Alessandretti et al., 2021). Even very low concentrations of DIC in the aquatic environment might be toxic to several organisms (Alessandretti et al., 2021). A similar phenomenon is observed for other NSAIDs (including NAP, IBP, ketoprofen (KET) and nimesulide (NIM)), which were present in the analysed wastewaters. These types of active substances might be substituted by meloxicam, which is considered to have a better safety profile than older NSAID agents (Evanon, 2007) or at least NAP might be used as a replacement, as it was recently shown to be a more environmentally friendly alternative than diclofenac (Näslund et al., 2020) (for details, please see Section 3.3).

APAP is one of the top-selling non-prescription drugs worldwide. Today, scientists pay attention to reducing its inadvertent overuse (Kaufman et al., 2019). Therefore, it is not surprising that it is also detectable in high amounts in wastewater (322 ngL<sup>-1</sup>), and low amounts in seawater (4.65 ngL<sup>-1</sup>) (Table 2). In comparison to other studies in the US and Europe, it was quantified in influent wastewater at 2–43 mgL<sup>-1</sup> and in effluent wastewater at 0.025–4.3 µgL<sup>-1</sup> (Al-Kaf et al., 2017). APAP is not bioaccumulative or toxic to aquatic organisms, and hence is not considered to be environmentally persistent (Peake et al., 2016). Nevertheless, the lack of information about the environmental behaviour of its metabolites and transformation products suggests that we should be cautious before emitting it into particularly sensitive environments such as the polar regions.

For KCZ, which is an azole antifungal, no traces were detectable after wastewater discharge. This compound has broad-spectrum fungicidal properties and is widely applied in shampoos, creams, gels and tablets to treat skin infections caused by a fungus (e.g., *paracoccidioidomycosis*, *chronic mucocutaneous candidiasis*, *coccidioidomycosis* and *histoplasmosis*). KCZ has an excretion rate in urine of ca. 13%, high permeability and a low solubility

**Table 1**

Concentrations of PPCPs and other emerging contaminants (ECs) in whole water analysis of wastewater and seawater samples collected during field campaigns in 2017 and 2019 (substance not detected – no shading; <MQL – pale grey; >MQL – dark grey).

PPCP or EC type	PPCPs and other EC concentrations in ngL <sup>-1</sup>											
	PPCPs										Other ECs	
	Antibiotics	Anticonvulsants	Beta-blockers	Nonsteroidal anti-inflammatory drugs		Angiotensin receptor blockers	Intermediate-acting benzodiazepine	Azole antifungals	Antidepressants	Systemic insecticide	Corrosion inhibitors, ultraviolet light stabilisers for plastics	Plasticiser
Sample name/substance name	<i>Trimetoprim</i>	<i>Carbamazepine</i>	<i>Metoprolol</i>	<i>Diclofenac</i>	<i>Naproxen</i>	<i>Losartan</i>	<i>Oxazepam</i>	<i>Ketoconazole</i>	<i>Venlafaxine</i>	<i>Imidacloprid</i>	<i>Benzotriazole</i>	<i>Bisphenol A</i>
Substance abbreviation	<i>TRI</i>	<i>CBZ</i>	<i>MET</i>	<i>DIC</i>	<i>NAP</i>	<i>LST</i>	<i>OZ</i>	<i>KCZ</i>	<i>VEN</i>	<i>IMD</i>	<i>BTA</i>	<i>BPA</i>
MQL (wastewater and seawater)	0.6	0.2	2.0	2.1	9.0	0.7	0.7	12.1	1.0	1.3	1.0	10
<b>2017</b>												
wastewater	N/F	N/F	N/F	74	2653	N/F	N/F	760	N/F	N/F	6340	N/F
seawater before discharge	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	71.6
Seawater_0h	N/F	N/F	N/F	2.9	N/F	N/F	N/F	N/F	2.0	N/F	N/F	98.3
Seawater_2h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_24h	N/F	N/F	N/F	3.8	6.8	N/F	N/F	N/F	N/F	N/F	N/F	76.0
<b>2019</b>												
wastewater	5	9	3	747	662	2	5	N/F	11	5	72	N/F
seawater before discharge	N/F	N/F	N/F	0.1	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_0h	N/F	N/F	N/F	0.1	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_1h	N/F	N/F	N/F	7.3	N/F	N/F	N/F	N/F	<1.0	N/F	N/F	N/F
Seawater_2h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_24h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_48h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_96h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Blank <sup>a</sup>	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F

Table 2

Concentrations of PPCPs in the dissolved phase of wastewater and seawater collected during the field campaign in 2019 (substance not detected – no shading; <MQL – pale grey; >MQL – dark grey).

PPCP or EC type	PPCP concentrations in ngL <sup>-1</sup>											
	Antibiotics	Analgesics and muscle relaxants			Anticonvulsants	Antihistamines	Anaesthetics	Antidiarrheals	Antidiabetics	Beta-blockers	β2 adrenergic receptor agonist	
Substance name	<i>Clindamycin</i>	<i>Trimethoprim</i>	<i>Isoniazide</i>	<i>Acetaminophen</i>	<i>Carbamazepine</i>	<i>Cetirizine</i>	<i>Lidocaine</i>	<i>Loperamide</i>	<i>Metformin</i>	<i>Atenolol</i>	<i>Carvedilol</i>	<i>Salbutamol</i>
Substance abbreviation	<i>CLI</i>	<i>TRI</i>	<i>INH</i>	<i>APAP</i>	<i>CBZ</i>	<i>CET</i>	<i>LD</i>	<i>LO</i>	<i>MFN</i>	<i>ATEN</i>	<i>CAR</i>	<i>SBS</i>
MQL (wastewater/seawater)	50/30	0.03/0.03	25/50	1.2/1.3	0.7/0.7	2/14	0.1/4.2	0.9/4.3	1.2/10	0.1/0.06	0.1/0.1	10/10
Sample name												
wastewater	<MQL	1.99	<MQL	332	<MQL	<MQL	<MQL	13.5	2.58	<MQL	N/F	<MQL
Seawater_0h	N/F	2.93	N/F	4.65	N/F	N/F	N/F	N/F	N/F	N/F	<MQL	N/F
Seawater_1h	N/F	N/F	N/F	<MQL	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_2h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_24h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_48h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
Seawater_96h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F
PPCP type	Cardiovascular agents	Insect repellent	UVA/UVB filters		Lipid regulators	Nonsteroidal anti-inflammatory drugs				Stimulant	Boosting supplement	
Sample name/substance name	<i>Methyldopa</i>	<i>N,N-Diethyl-met-toluamide</i>	<i>para-aminobenzoic acid</i>	<i>benzophenone 1</i>	<i>Atorvastatin</i>	<i>Ibuprofen</i>	<i>Nimesulide</i>	<i>Ketoprofen</i>	<i>Diclofenac</i>	<i>Caffeine</i>	<i>Caffeic Acid</i>	
Substance abbreviation	<i>MDOP</i>	<i>DEET</i>	<i>PABA</i>	<i>BP-1</i>	<i>AT</i>	<i>IBP</i>	<i>NIM</i>	<i>KET</i>	<i>DIC</i>	<i>CAF</i>	<i>CA</i>	
MQL (wastewater/seawater)	35/35	0.1/0.2	6.8/16.7	0.4/1.3	1.7/45.5	50/30	10/0.2	0.5/0.5	5/5.1	0.5/0.17	10/1.4	
Sample name												
wastewater	7.84	6.21	17.7	4.48	7.67	477	N/F	14.61	19.4	3310	<MQL	
Seawater_0h	N/F	<MQL	N/F	<MQL	N/F	<MQL	17.1	4.47	<MQL	49.9	N/F	
Seawater_1h	N/F	<MQL	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	
Seawater_2h	N/F	<MQL	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	
Seawater_24h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	
Seawater_48h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	
Seawater_96h	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	N/F	

Abbreviations: N/F – not found (<MDL); MDL – method detection limit; MQL – method quantification limit;

in water (Zadaliashgar et al., 2020), which explains why it was not detected in water samples. (In all samples it was below detection limits.)

CBZ is a widely used prescription anti-epileptic drug. Based on (Ternes et al., 2004) the pharmaco-kinetical excretion rate is only 1–2% in unchanged form. More recent research by (Verlicchi and Zambello, 2016) summarised several different sources of excretion rates and concluded that it is sometimes difficult to identify such data. Verlicchi and Zambello (2016) indicated both an interval for excretion rates between 1 and 61%, and an average of 31%. CBZ has been found in wastewater samples collected both in 2017 (9 ngL<sup>-1</sup>) and in 2019 (<method quantification limit) (Verlicchi and Zambello, 2016). No traces were detectable in seawater, however. Other studies performed in Antarctica also show CBZ results below the method quantification limit (González-Alonso et al., 2017). However, we still suggest monitoring its presence due to the negative environmental consequences after chronic exposure (Ferrari et al., 2003). Recently, researchers investigated both the acute and chronic effects of carbamazepine on *Daphnia similis* (a relative of the more well-known *Daphnia magna*) (Chen et al., 2019). For example, after 21 days of the chronic trials, a reduced number of offspring per litter was observed already at concentrations as low as 30 ngL<sup>-1</sup>, while the total number of offspring per female decreased at 3000 ngL<sup>-1</sup>. Other researchers exposed two marine species to CBZ at different concentration levels for 28 days (Freitas et al., 2015); the mussel *Scrobicularia plana*; and the ringworm *Diopatra neapolitana*. The experiments analysed different biochemical responses in the animals and were able to show that CBZ caused oxidative stress and cell damage at a concentration of 9000 ngL<sup>-1</sup>.

Antibiotics comprise a group of compounds known as antimicrobial agents. In this group, three compounds were identified in the wastewater samples: (1) trimethoprim (TRI), which is commonly applied during medical treatment together with sulfamethoxazole (SUL), was found at 1.99 ngL<sup>-1</sup> in the dissolved phase and 5 ngL<sup>-1</sup> in total water analysis; (2) clindamycin (CLI), which is a bactericidal agent, was found in concentrations <50 ngL<sup>-1</sup>; and (3) isoniazide (INH) is used for treatment of tuberculosis and was found in concentrations <25 ngL<sup>-1</sup>. The World Health Organisation (WHO) has a rising concern that antibiotics constitute a growing threat to world communities due to the development of antibiotic-

resistant bacteria (Fatta-Kassinos et al., 2011). This phenomenon is discussed in more detail in Section 3.2 and includes a description and analysis of our preliminary studies of the presence of antibiotic resistant genes in the water samples.

UVA/UVB filters are used to protect skin against sunburns, premature skin ageing and the risk of developing skin cancer. They are identified as ECs due to their persistence in the environment, potential to accumulate in biota and possible threat as endocrine disruptors (Ramos et al., 2016). Using UVA/UVB filters as protection is especially necessary in the South Pole region, where the stratospheric ozone layer decreased beginning in the mid-1980s due to the presence of chlorofluorocarbons (CFCs). Despite evidence now emerging that the ozone hole in the Antarctic zone is recovering (Bernhard and Stierle, 2020), special skin protection is still required. Para-aminobenzoic acid (PABA) was found in the wastewater samples from 2019 at a concentration 17.7 ngL<sup>-1</sup>, while benzophenone 1 (BP-1) was quantified at 4.48 ngL<sup>-1</sup>. The other representatives of this group (not detected under present study) reported in (Ramos et al., 2016), such as benzophenone 3 (BP-3) and benzophenone 4 (BP-4), tend to accumulate in wastewater up to a few mgL<sup>-1</sup>; hence, application of BP-1, BP-3, BP-4 in remote polar areas needs to be limited to a minimum and/or their emission mitigated using advanced technologies.

Traces of angiotensin receptor blockers, intermediate-acting benzodiazepine, antidepressants, antidiarrhoeals, antidiabetics, cardiovascular agents, lipid regulators, cardiovascular agents, insect repellents and systemic insecticides were also determined at trace levels (<14 ngL<sup>-1</sup>). For other groups of PPCPs including antihistamines, anaesthetics, beta-blockers, β2 adrenergic receptor agonists and boosting supplements, the concentrations in wastewater and seawater were mostly below method quantification limit (MQL) or not detected (for details, see Tables 1 and 2).

As regards to other ECs, benzotriazole (BTA) and bisphenol A (BPA) are drawing attention due to their presence in the Antarctic environment: 72–6340 ngL<sup>-1</sup> for BTA in wastewater and 71.0–98.3 ngL<sup>-1</sup> in seawater. Both belong to the group of chemicals known as endocrine disruptors and were previously identified in the northern Antarctic Peninsula region in concentration ranges of <0.07–17.71 ngL<sup>-1</sup> in fresh water (streams) and 172 ngL<sup>-1</sup> in untreated wastewater for BTA and <0.12–18.74 ngL<sup>-1</sup> in



fresh water (streams) and  $<0.12 \text{ ngL}^{-1}$  in untreated wastewater for BPA (Esteban et al., 2016). Benzotriazoles are used as anticorrosive agents in cleaning products for dishwashing and might be used as intermediaries for colorants, pharmaceuticals and fungicides. Benzotriazole (1H-benzotriazole) is also used as an antifreeze, in heating and cooling systems and in de-icing fluids for aircraft. There are several possible pathways for its dissemination to the Antarctic environment, but, wastewater is considered as the main emission source (Careghini et al., 2015). In turn, BPA is a key monomer in the production of plastics (epoxy resins, flame retardants etc.) and is used as an additive in thermal papers and paper coatings (Fuerhacker, 2003). Moreover, even though BPA showed weak estrogenic activity (Fuerhacker, 2003) it belongs to Category 1 of the Endocrine Disrupter Priority List (Petersen et al., 2007) for wildlife and human health. Based on our study (Table 1), it is not detectable in wastewater, but quantifiable in seawater. This might be related to the strong matrix effects in wastewater, where it is not possible to detect BPA below  $10 \text{ ngL}^{-1}$ . Besides that, external sources of BPA (excluding untreated wastewater) might also be possible.

### 3.2. Antimicrobial resistance

The worldwide increase in bacterial resistance is indicated to be a consequence of the extensive use of antimicrobial agents in medical practice (Dodd, 2012), and nonmedical usage such as: veterinary, aquaculture, agriculture, and animal growth promotion. Additionally, numerous domestic products (e.g., detergents, cleaning chemicals, cosmetics) have antibacterial, antifungal and antiviral properties, which may co-select for antimicrobial resistance. Since the level of bacterial resistance has been mainly attributed to anthropogenic activity, the geographically isolated Antarctica has been considered as a pristine area, where bacteria harbouring resistance genes can be disseminated to some extent, mainly by migrating birds/animals (having direct contact with humans) and by research activity (Bonnedahl et al., 2008; Gordon and Cowling, 2003). However, the recent considerable increase in tourism and scientific investigation in Antarctica (Bonnedahl et al., 2008; Cowan et al., 2011) could affect the local environmental niches, including the bacterial resistome.

This study tries to shed light on the presence and distribution of integrons (int 1–3) and sulphonamide resistance genes (sul 1–3) in the total microbial community at a wastewater discharge point in Admiralty Bay. Importantly, the sulphonamide group consists of synthetic antimicrobial agents; thus, sul genes are directly linked with human activity. Similarly, integrons, especially class-1 integron-integrase gene (int 1), were suggested as a generic marker of anthropogenic pollution (Gillings et al., 2015). To assess the level of resistance proportional to the size of the overall population detected in the tested samples, the obtained numbers of quantified copies of the sul 1–3 and int 1–3 genes were plotted normalised to the number of copies of Bacterial 16S rRNA genes (Fig. 2). According to the obtained results, the total number of copies of Bacterial 16S rRNA genes was found to be consistent between samples, except the discharge, where it was two times higher. Interestingly, sul 1 and sul 2 were detected together with the int 1 gene in each sample, even prior to discharge, which characterised the background level of resistance (Fig. 2). Indirectly, it also indicated that microbial populations may retain resistance genes, even after the discharge event, in the area of the periodical discharge of wastewater (according to personal communication, the frequency of discharge during the summertime is about every 2–4 weeks). All tested resistance genes and integrons were found at discharge time (seawater 0 h), with the highest concentration of sul 1 and int 1 ( $4.2 \times 10^{-2}$  and  $9.6 \times 10^{-5}$  copy genes/copy of 16S rRNA genes, respectively). With time, the concentration of tested genes in general decreased except for int 2, whose highest level was noted 2 h after discharge ( $2.1 \times 10^{-4}$  copy genes/copy of 16S rRNA genes). Our results agree with other studies suggesting a strong correlation of int 1 and sul 1 in wastewater (Wang et al., 2014). It is estimated that up to 80% of human-related enterobacteria may be equipped with class-1 integrons (Tenailon et al., 2010); thus, a large number of them might be realised to wastewater and then (depending on wastewater treatment efficiency) to

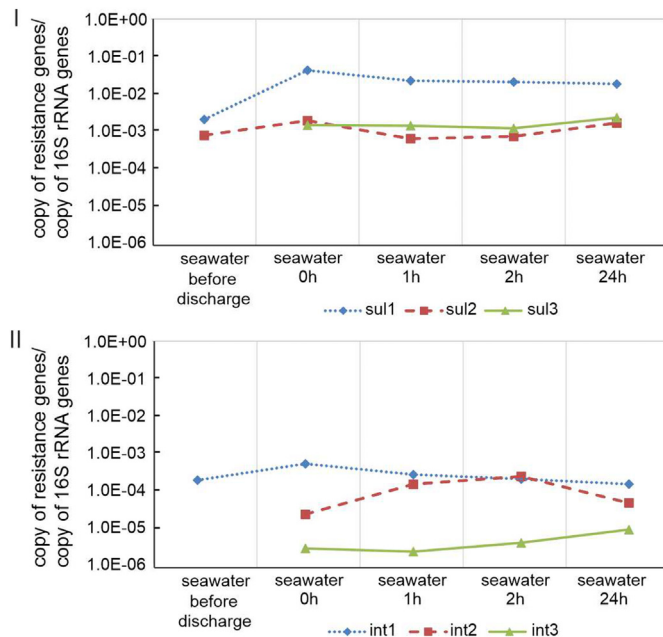


Fig. 2. Copies of resistance genes: (I) sul 1–3 (II) int 1–3, normalised to the number of Bacterial 16S rRNA genes prior to, during and at a certain time after the discharge of wastewater to Admiralty Bay.

the receiver (Gillings et al., 2015). It is, however, suggested that abundance of int 1, and resistance in general, may even increase during the wastewater treatment process as a result of selecting pressure driven by antimicrobial agents, heavy metals, surfactants and others (Gillings et al., 2015). This is of high concern since, in this study, the residuals of antimicrobial agents and other pharmaceuticals were detected in wastewater generated at Arctowski Station. Since there is a lack of such data, further investigation is needed to determine whether and how the quality of wastewater and of the receiver is linked with the presence, distribution, transfer and persistence of resistance genes. Monitoring of changes in the resistome of polar regions can provide important data for the holistic “One Health” approach, which aims to recognise and solve health threats at the human–animal–environment interface.

### 3.3. Environmental risk assessment for selected PPCPs and other ECs

Up to now, there is no environmental guideline procedure for the reduction of harmful contaminant emissions in Antarctica. Nevertheless, the current US and European regulatory guidance might be applied (de Bruijn and ten Heuvelhof, 2002). This regulation required new pharmaceuticals to undergo standard toxicity tests using algae, invertebrates (e.g., *Daphnia magna*) and fish if the predicted or measured environmental concentration (PEC or MEC) of the active species is  $>1 \mu\text{gL}^{-1}$  (US legislation) or  $10 \text{ ngL}^{-1}$  (European Medicines Agency). Considering that Antarctic trophic webs have a simple structure and the detoxification mechanisms in the particular organisms are not yet fully understood (Corsolini, 2009), we decided to apply the lowest PNEC obtained for marine organisms based on the NORMAN Ecotoxicology Database and available literature data (Minguez et al., 2016) to evaluate potential environmental risks (Risk Quotients, RQ) to the marine environment posed by wastewater discharged to Admiralty Bay. The results for the highest value of MEC of the detected ECs at a level exceeding  $10 \text{ ngL}^{-1}$ , together with the calculated RQs are presented in Table 3.

The RQ [wastewater] values obtained show that KET, NAP, NIM and PABA pose a low risk for marine species. Among the nonsteroidal anti-inflammatory drugs, NAP has the highest concentration in wastewater, but also the highest PNEC value, at  $4440 \text{ ngL}^{-1}$ . Hence, it is suggested to apply this rather than the nonsteroidal anti-inflammatory drug DIC as

**Table 3**

Environmental risk assessment – Risk Quotients (RQ) associated with non-treated wastewater discharge in Admiralty Bay. Environmental risk levels description: RQ: <0.1 – insignificant (blue); RQ: 0.1–1.0 – low (green); RQ: 1.0–10 – moderate (yellow); RQ: >10 – high (red).

PPCP and other EC class	Contaminant species	Max detected concentration in wastewater [ngL <sup>-1</sup> ]	Max detected concentration in marine water [ngL <sup>-1</sup> ]	Marine organisms name (parent category) if available	PNEC [ngL <sup>-1</sup> ]	Risk Quotients [wastewater] value/risk	Risk Quotients [marine water] value/risk	References
<b>Pharmaceuticals</b>								
Analgesics and muscle relaxants	Acetaminophen	332	<10	Pimephales promela (fish)	81.4	4.08	-	(Minguez et al., 2016)
				not specified	13400	0.02	-	NORMAN Ecotoxicology Database
Antidiarrhoeals	Loperamide	13.5	N/F	not specified	4	3.38	-	NORMAN Ecotoxicology Database
Azole antifungals	Ketoconazole	760	N/F	Skeletonema marinoi (diatom)	4.57	166	-	(Minguez et al., 2016)
				not specified	0.81	938	-	NORMAN Ecotoxicology Database
Antidepressants	Venlafaxine	11.0	<10	Skeletonema marinoi (diatom)	322	0.03	-	(Minguez et al., 2016)
				not specified	3.8	2.89	-	NORMAN Ecotoxicology Database
Nonsteroidal anti-inflammatory drugs	Ibuprofen	477	30	not specified	100	4.77	0.3	NORMAN Ecotoxicology Database
	Nimesulide	17.1	17.1	not specified	140	0.12	0.3	NORMAN Ecotoxicology Database
	Ketoprofen	16.6	<10	Artemia salina (Crustacea)	1324	0.01	-	(Minguez et al., 2016)
				not specified	210	0.08	-	NORMAN Ecotoxicology Database
	Diclofenac	747	<10	Pseudokirchneriella subcapitata (microalgae)	2130	0.35	-	(Minguez et al., 2016)
				not specified	5	149	-	NORMAN Ecotoxicology Database
Naproxen	2653	<10	Pseudokirchneriella subcapitata (microalga)	4440	0.60	-	(Minguez et al., 2016)	
<b>Personal Care Products</b>								
UVA/UVB filters	4-aminobenzoate (PABA)	17.7	N/F	not specified	2370	0.01	-	NORMAN Ecotoxicology Database
Stimulant	Caffeine	3310	49.9	not specified	120	27.6	0.4	NORMAN Ecotoxicology Database
<b>Other ECs</b>								
Corrosion inhibitors, UV light stabilisers for plastics	Benzotriazole	6340	N/F	not specified	780	8.13	-	NORMAN Ecotoxicology Database

already suggested by (Näslund et al., 2020). This will help to minimise the possible environmental consequences of using pharmaceuticals from this group. For UV filters, similar results are observed by (Olalla et al., 2020). The authors concluded that this group did not present an environmental risk at the presented concentrations. Nevertheless, they emphasised that, due to their lipophilic properties, they may bioaccumulate, and their concentrations are recommended to be monitored in the Antarctic environment (Olalla et al., 2020).

In the case of APAP, loperamide, venlafaxine, IBP and BTA, we can conclude that the measured concentrations detected pose a moderate risk to aquatic marine life. According to Olalla et al. (2020), acetaminophen has also been identified as high risk in wastewater discharges, but we do agree with the authors that the risk posed by this compound will be lower after dilution.

Regarding IBP, a moderate RQ can be noted, and recent studies suggest that exposure to it may affect the oxidative stress response, osmoregulation and the synthesis of hormones involved in the reproduction of aquatic organisms (Jeffries et al., 2015). Hence, their emission in such environments needs to be reduced. Moreover, considering not only the moderate RQ for BTA, but also its limited biodegradability and carcinogenic properties (Esteban et al., 2016), its emission should also be strongly limited.

Finally, the highest attention should be paid to KCZ, DIC and CAF, since their detected concentrations pose a high risk to marine species (Table 3).

KCZ, together with other azole compounds, is commonly detected in the environment and may have several detrimental effects on fish (Bhagat et al., 2021). Current knowledge and studies reporting adverse biological effects of azole on fish (Bhagat et al., 2021), and the RQ result presented in Table 3 call for better management of these ECs.

As underlined before, diclofenac belongs to the NSAIDs, and many studies highlight this compound (Ferrari et al., 2003; González-Alonso et al.,

2017; Olalla et al., 2020) due to its possible negative consequences in the environment. Table 3 shows that for microalgae the risk will be low but considering the lowest available NOEC for a marine environment, the risk increases to high, and the RQ exceeds the limit more than tenfold. Unfortunately, the weather conditions in polar regions are conducive to the use of such pharmaceuticals, which consequently results in increased emission during the most intense anthropogenic activities (Olalla et al., 2020). In contrast to (Olalla et al., 2020), the RQ for CAF (Table 3) shows a high risk to the marine environment. This compound is decidedly the most commonly detected lifestyle compound in water as a result of anthropogenic activity (Stefanakis and Becker, 2015). Despite this compound's capacity to disorder environmental stability, it is also biodegradable, and, by introducing a bioremediation step, CAF can be substantially reduced prior to discharge of wastewater to the environment (Ibrahim et al., 2014).

It should be noted that the presented results (Table 3) take into consideration the number and typology of standard ecotoxicological tests (and recommended organisms) and commonly these do not include organisms from extreme habitats such as Antarctica. On the other hand, RQ calculation in marine water (Table 3) shows insignificant influence of determined micropollutants, except IBP, NIM and CAF (RQ shows low risk). This indicates proper dilution factor in the sampling point. However, we need to emphasise that the RQ for such a pristine environment might be even more worrying than those presented in this article. Slow degradation processes, accumulation of micropollution and continuous wastewater discharge may have great impact on RQ increase in the marine environment. To understand the problem of occurrence of ECs in the Antarctic ecosystem, broader and more prolonged monitoring of targeted pollutants is needed. This would help firstly in selecting the general markers for monitoring among all Antarctic stations, and secondly in taking action to mitigate the influence of pollutant emissions. What is more, pollution sources vary



greatly, and mitigation is a great challenge. However, by considering point sources like wastewater discharges there is a great possibility to reduce contaminants using end-of-pipe technologies described for in detail for e.g. in Szopińska et al. (2021).

#### 4. Conclusion

This is the first study describing the presence of a wide range of PPCPs and other emerging contaminants, including illegal drugs in the water and wastewater samples collected in the surroundings of the Arctowski Station (western shore of Admiralty Bay), using a risk quotient (RQ) calculation to identify their environmental risk. This analysis has allowed us to identify the presence of 34 PPCPs and other ECs from among the more than 170 substances analysed. It needs to be noted that in Antarctica no systematic data on the pharmaceutical profile (medication for regular use, or medication for occasional use) of the human population is monitored. As seen from our study, many of these substances are excreted into the wastewater and ultimately reach the aquatic environment after discharge. Hence, it is suggested to create a centralised record of the medication prescribed and consumed in situ. Moreover, it is recommended, when possible to use more environmentally friendly substitutes for both pharmaceuticals and personal care products (limiting consumption at the source).

Additionally, based on the presented results we are calling for a wider monitoring of PPCPs among other stations, and the enhancement of mitigation actions to reduce their emission to the Antarctic aquatic environment by the installation of more advanced wastewater treatment systems (end-of-pipe-technology). Candidate markers for continuous monitoring needs to be selected after a preliminary screening of a wide range of PPCPs/ECs at each station. However, compounds as acetaminophen, diclofenac, ibuprofen, and caffeine seem to occur at several scientific stations and may be good first candidates for a more regular monitoring at (or near) some of the 82 stations in the Antarctic.

The presence of ARGs in polar regions may raise a lot of concerns. On the other hand, the detailed analysis of resistome changes in polar regions can provide important data to inform the global holistic view to recognise and solve health threats at the human-animal-environment nexus.

Considering the results presented above, a potential further line of Antarctic research and activities to alleviate our understanding of anthropopressure can be to: (1) perform more permanent monitoring of PPCPs and other ECs (consumption and environmental measures), (2) perform more detailed analysis of the antimicrobial resistance phenomenon, (3) limit the use of those PPCPs and other ECs detected at the greatest concentrations and (4) install more advanced systems for wastewaters treatment (end-of-pipe-technology).

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#### CRedit authorship contribution statement

**Małgorzata Szopińska:** Conceptualization, Methodology, Investigation, Validation, Visualization, Writing - Original Draft, Review & Editing, Main project administration, Funding acquisition. **Joanna Potapowicz:** Investigation, Writing - Review & Editing, Funding acquisition. **Katarzyna Jankowska:** Conceptualization, Visualization, **Aneta Luczkiewicz:** Conceptualization, Writing - Review & Editing. **Ola Svahn:** Investigation,

Writing - Review & Editing. **Erland Björklund:** Investigation, Writing - Review & Editing. **Christina Nannou:** Investigation, Writing - Review & Editing., **Dimitra Lambropoulou:** Investigation, Funding acquisition, Writing - Review & Editing, **Żaneta Polkowska:** Supervision.

#### 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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.155400>.

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