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First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica)

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ABSTRACT

In Antarctica, waste is generated mainly during scientific research programmes and related logistics. In this study, the impact of wastewater on the western shore of Admiralty Bay was investigated during austral summer in 2017 and 2019. A range of physicochemical parameters and the presence of selected trace metals, formaldehyde and different groups of surfactants were determined in wastewater coming from Arctowski Station and in nearby coastal waters. The presence of selected trace metals (e.g., Cr: 2.7-4.4 µg/L; Zn: 15.2-37.3 µg/L; and Ni: 0.9 - 23.3 µg/L) and the sums of cationic (0.3-1.5 mg/L), anionic (3.1-1.7 mg/L), and non-ionic (0.6-2.4

mg/L) surfactants in wastewater indicated the potential influence of anthropogenic factors on sea water. The determined surfactants are found in many hygiene products that end up in the waste water tank after human use and, if untreated, can be released into surface waters with discharge. In addition, the levels of some trace metals indicate that they cannot come only from natural sources, but are the result of human activity. The reported data show disturbances in the marine environment caused by non-treated wastewater discharge, *e.g.* by comparing the obtained results from the values of the no observed effect concentrations (NOECs) on selected Antarctic bioindicators, and provide information for the implementation of proper wastewater treatment at any Antarctic station in the future.

GRAPHICAL ABSTRACT

1. Introduction

Antarctica has unique value, as it is an international territory designated for peaceful and scientific purposes (The Antarctic Treaty, 1959). However, signs of anthropogenic activity in Antarctica have been visible since the 1960s (Sladen et al., 1966). The environmental consequences of human activities (both scientific and touristic) have been documented by several authors (Bargagli, 2008; Benninghoff and Bonner, 1985; Corsolini, 2009; Szopińska et al., 2017, Potapowicz et al., 2019), indicating different sources of pollution, such as atmospheric deposition and diesel fuel combustion; however, recently, waste and wastewater management have gained increasing concern (Connor, 2008, KumarBharti et al., 2016). Improper wastewater discharge in pristine Antarctic marine water may introduce not only persistent organic pollutants and other emerging organic and inorganic contaminants but also non-indigenous microorganisms, including human-associated pathogens and viruses (Tort et al., 2017).

To date, no continent-wide wastewater quality discharge guidelines have been developed and accepted by the countries operating bases and claiming territory in Antarctica. Annex III (Waste Disposal and Waste Management) of the Protocol on Environmental Protection to the Antarctic Treaty (hereafter, the Protocol) requires countries to preserve the environment for future generations (The Protocol on Environmental Protection to the Antarctic Treaty). It is therefore necessary to develop proper waste management plans. Annex III requires that all wastes produced or disposed of in the Antarctic Treaty area have limited negative impact on the environment. All liquid wastes, including domestic wastewater, need to be removed from the Antarctic Treaty area to the maximum practicable extent (Article 2, Annex III of the Protocol). Only if proper dilution and rapid dispersion are ensured can wastewater be discharged directly into marine waters (Article 5, Annex III), but this requirement is rather vague because no definitions were given for key terms, such as “assimilative capacity”, “initial dilution” or “rapid dispersal”. Investigation of the impact of continuous wastewater disposal into Antarctic marine water ecosystems has been relatively limited. A few stations, such as McMurdo (Conlan et al., 2004; Lenihan and Oliver, 1995) and Davis (Stark et al., 2016, 2015) stations, have focused directly on this topic. The wastewater influence on the marine water quality of Admiralty Bay has been studied since 1997, e.g., research conducted at the Martel Inlet (Martins et al., 2005, 2002; Montone et al., 2010) and also shows the favoured dispersion of wastewater at the discharge points, which is caused by local hydrodynamic conditions, especially tides (Montone et al., 2010). However, at the same time, some chemical indicators (such as sterols and linear alkylbenzenes) have been found in marine sediments (Martins et al., 2005, 2002), indicating contamination by continuous wastewater discharge. Combined evidence of environmental impacts caused by wastewater discharge from the Davis Station, East Antarctica (non-native microbiota and antibiotic resistance determinants in sediments, water in marine benthic communities, and histopathological abnormalities in local fish species), was also presented by Stark and co-authors (Stark et al., 2016).

In the area of current interest, Admiralty Bay, wastewater influence on ecosystems has been reported only in terms of microbiological pollution (faecal bacteria), presence of sterols and linear alkylbenzenes (Martins et al., 2005, 2002), while wastewater discharge from the Arctowski Polish Antarctic Station (western shore of Admiralty Bay) has not been investigated. Previous studies have confirmed that sewage discharges in the Antarctic area can cause environmental impacts on the local marine ecosystem and pose a risk of environmental degradation (Martins et al., 2005, 2002; Stark et al., 2016, 2015). Thus in this study, the dispersal and distribution of wastewater after discharge into the receiving environment (Admiralty Bay) was examined in 2017 and 2019 using measurements of nutrients, organic matter, trace metals (Pb, Fe, Cd, Zn, Cu, Ni, Co, and Cr), different groups of surfactants (non-ionic-SNI, cationic-SC and anionic-SA), and formaldehyde concentrations. Principal component analysis (PCA) was performed to observe potential correlations which provide valuable information on the environmental fate of the chemical pollutants under study. In our work we described in detail chemical disturbances in Admiralty Bay after wastewater discharge. The main purpose of this study was an initial risk assessment given that the data obtained can be used for this purpose. Risk assessment has been evaluated by comparing the obtained results from the values of the no observed effect concentrations (NOECs) on selected Antarctic bioindicators. This type of research and data evaluation has been conducted for the first time in the vicinity of Arctowski Station, and the results may thus constitute baseline conditions for any future anthropogenic impact assessment. Moreover, our research confirms that the proposed set of contaminants, which can be determined by simple analytical procedures (including spectrophotometric methods), may be considered suitable for routine analysis in Antarctica to monitor compliance with environmental regulations. .

2. Material and methods

2.1 Arctowski Station wastewater system and sampling design

The study area is located on the western shore of Admiralty Bay (King George Island, South Shetland Islands, Fig. 1A) in a small ice-free area on the north-eastern tip of the Warsaw Icefield. Arctowski Station (62°09′34″S, 58°28′15″W; Fig. 1B), which was built in 1977, consists of a facility with fifteen separate buildings. The maximum population during the peak season (summer) at the station may reach 37 persons (Supplementary Material, Table S1). These people conduct scientific research and other activities connected with maintenance of the station. During the winter season, there are only 8 persons on the staff who are responsible for station maintenance and the long-term monitoring programmes (i.e., programmes in ecology, hydrology, oceanography, chemistry, and glaciology). Due to the freezing of surface waters, supplying the station with drinking and hygiene water (freezing of the lake from which the water is pumped) and wastewater disposal (freezing of the bay - place of discharge) are especially challenging during the winter season. Daily water consumption at Arctowski Station during the period 2016-2019 was relatively low (149 L per person per day, Supplementary Material, Table S1). Nevertheless, access to drinking and household water is limited due to the sustainable usage of natural resources and the need to stay below the daily limit of 230 L per person per day (Supplementary Material, Table S1, Fig. S1).

Water (glacial and snow melt water) is obtained from the lake located near the station, which is supplied by Petrified Forest Creek (see Fig. 1B and Fig. 1C). There is no wastewater treatment plant at the Arctowski Station. Wastewater (grey and black water) is collected and directed to four buried septic tanks. The first tank (A) is connected to the main building and laboratory; the second (B) covers technical facilities, including toilets, showers and laundry facilities; the third (C) is connected to summer houses; and the fourth (D) is connected to the building known as the meteorological station (Fig. 1C). The facility at the main building is limited primarily to treating non-solid waste (maceration). In the other buildings, no wastewater treatment is applied. There is no information regarding the total volume of each septic tank; however, the amount of produced wastewater is estimated to be in the range of 31.4 – 80.7 m^3 per year (Supplementary Material Table S1; Fig. 2). Water consumption in relation to the number of people present at Arctowski Station is presented in Fig. S2 (Supplementary Material).

The liquid residues of septic tanks are discharged to Admiralty Bay. The wastewater discharge point is at Point Thomas (62°10′S 58°30′W) on the south side of the entrance to Ezcurra Inlet in Admiralty Bay (Fig. 1 B, sampling point no. 1). This location and the depth of the bay, which is more than 550 m (Rakusa-Suszczewski, 1993), are expected to provide proper conditions for the "initial dilution" and "rapid dispersal" of discharged wastewater. Nonetheless, to date, no research concerning the possible contamination of local marine ecosystems has been conducted.

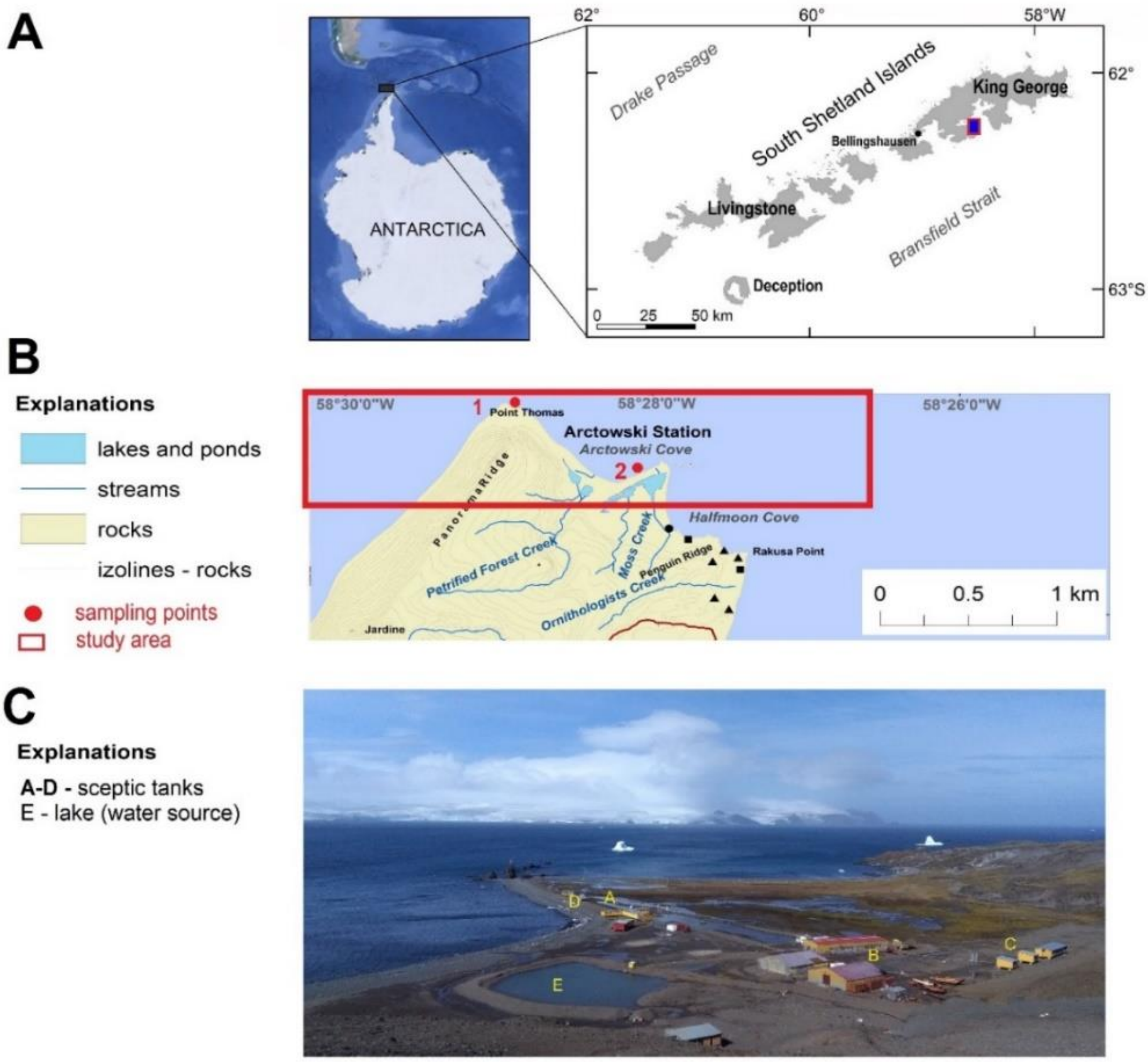

Figure 1. Location of the study area: A) location of King George Island in relation to Antarctica; B) location of Arctowski Station and sampling points; and C) location of Arctowski Station facilities and septic tanks (Figs. A and B are adapted from Szopińska et al., (2018))

In this study, wastewater and marine water samples were collected during two sampling campaigns conducted on 18-20 January 2017 and 1-5 April 2019. Wastewater was collected from septic tank A, which is connected to the main building and laboratory (see Fig. 1C). To analyse the dilution and dispersion of wastewater in the marine environment, the sampling points were placed in the discharge area (point no. 1) and near the lighthouse (point no. 2), approximately 1 km away from the discharge point. The samples were collected at regular time intervals after discharge: after 0.5 h, 1 h, 2 h, 24 h, 48 h and 96 h. Sampling at point no. 2 was not possible during 2019.

2.2 Sample analysis

After collection, all samples were transported to the Arctowski Station laboratory. Redox potential, pH and conductivity were measured using a HQ40d portable multimeter in the field. For other physical and chemical analysis, samples were stored frozen at -20°C and transported under unchanged temperature conditions to Poland. Before analysis all samples were allowed to thaw slowly overnight. Analysis included the determination of chemical oxygen demand (COD), inorganic nitrogen compounds ($N\text{-}NH_4^+$, $N\text{-}NO_3^-$, and $N\text{-}NO_2^-$), total nitrogen (TN), orthophosphate ($P\text{-}PO_4^{3-}$) and total phosphorus (TP) using spectrophotometric methods (*XION 500 spectrophotometer, Dr. Lange, GmbH, Germany*). To exclude chloride influence on COD analysis, the sample was diluted 10-fold. According to EN ISO 5667-3, samples for ammonium determination can be stored in plastic bottles up to one month in a freezer at below -18°C. Specific chemical analysis included trace metal (Pb, Fe, Cd, Zn, Cu, Ni, Co, and Cr) determination using inductively coupled plasma mass spectrometry (*Thermo XSERIES 2 ICP-MS).* Acidified samples were analysed without filtration – total concentration of each metal was recorded under the following conditions: collision gas (Ar) flow: 13 L min^{-1}; aux. gas flow: 0.7 L min^{-1}; nebulizer gas flow: 0.9 L min^{-1}; collision cell technology - CCT gas (8% Hydrogen in Helium) flow 5.5 mL min^{-1}, CCT mode +3 Kinetic Energy Discrimination. A multi-element ICP-MS standards mix 10 mgL^{-1} from Inorganic Ventures (Christiansburg, VA, USA) was used for calibration. Different groups of surfactants (SNI, SC and SA) and formaldehyde were determined using cuvette tests and a UV-VIS spectrophotometer *(Spectroquant Pharo 300 Merck, Germany)*. Biological oxygen demand in wastewater samples (5-day test, BOD_5) was measured using WTW OxiTop, OC 100.

All analyses were carried out according to the Good Laboratory Practice (GLP) requirements. The basic validation parameters of the methods used are presented in Supplementary Information, Table S4. LCK Cuvette Tests quality assurance is provided in certificates based on Analytical Quality Assurance (AQA) System in accordance with the American Public Health Association (American Public Health Association et al., 2005).

2.3 Statistical analysis

Applying the results from two sampling campaigns, a multivariate dataset was created, and Principal Component Analysis (PCA) was employed to reveal correlations in the data using MATLAB Version: R2020a with Statistics and Machine Learning Toolbox Version 11.7.

3. Results

3.1 General chemical characteristics

To assess the environmental impact related to wastewater deposition, wastewater generated at both Arctowski Station and the seawater collected near the discharge point (receiving environment) (Fig. 1B, no. 1) and the second sampling point (Fig. 1B, no. 2), were analysed. The properties of the collected samples are presented in Table S2, Supplementary Information and summarised in Table 1. According to physicochemical analysis, wastewater presented values similar to those produced in countries with low populations and cold climates (Table S2, Supplementary Material), such as Norway (Pons et al., 2004). The BOD_5 values tested only in wastewater were 1099 mgO_2/L in 2017 and 806 mgO_2/L in 2019, with a BOD_5/COD ratio of 0.46-0.58, indicating that half of the organic matter is amenable to biodegradation. In seawater samples collected immediately after wastewater discharge, the COD value equalled 58.6 mgO_2/L in 2017 and 75.4 mgO_2/L in 2019. After 24 h, the COD decreased back to the values measured before discharge (Table S2, Supplementary Material). In the case of pH, conductivity and redox value, their minor fluctuations can be the result of sea currents rather than wastewater disposal. In terms of nutrient dispersion, the concentration levels of phosphorus and nitrogen compounds reverted in sea water to the values before discharge within two hours. Additionally, no significant changes in phosphorus and nitrogen compound concentrations at point no. 2 were observed (Table S2, Supplementary Material).

3.2 Selected micropollutants analysis

The presence of trace metals (Table S3, Supplementary Material) and selected organic micropollutants, such as formaldehyde and the sums of cationic (SC), anionic (SA), and non-ionic (SNI) surfactants (Fig. S2, Supplementary Material), were also analysed in wastewater and receiving waters. An increase in Zn concentration in seawater samples after wastewater discharge was noticeable in 2017 at both the second (up to 8.42 µg/L) and first (up to 3.04 µg/L) sampling points (see Table S3, Supplementary Material). In 2019, an increase in Zn concentration after wastewater discharge was also observed (increase from 0.19 µg/L before discharge to 0.98 µg/L after discharge). Nevertheless, the Zn concentration in wastewater in 2017 was approximately two times lower than that in 2019. However, an increase in Fe concentration in seawater directly after discharge was also observed (from 0.54 to 2.01 µg/L in 2017 and from 3.31 to 24.42 µg/L in 2019), and it decreased within the sampling time to 0.39 in 2017 and 0.24 µg/L in 2019. Pb was present in wastewater at concentrations of 0.48 µg/L in 2017 and 0.14 µg/L in 2019; however, it was below the detection limit (< 0.01 µg/L) in seawater, even directly after wastewater discharge. A similar phenomenon was observed for Cd and Co during both sampling campaigns. In wastewater samples in 2017 and 2019, concentrations ranged between 0.03-0.45 µg/L (Cd) and 1.68-2.13 µg/L (Co), while in the seawater samples after 24 h, Cd and Co concentrations were up to 0.02 µg/L. Regarding Ni, lower concentrations during the 2019 sampling campaign were observed in both wastewater and marine water (Table S3, Supplementary Material). For Cu an increase in concentration in wastewater and its receiver in sampling area no. 1 was observed between 2017 and 2019.

However, no visible trend (e.g., decrease in concentration in time after discharge) was observed during the 2019 sampling campaign.

Considering the toxicological properties of the analysed parameters (Kowalik, 2011; Olkowska et al., 2011; Thornton et al., 2001), the results have been assessed in relation to the available literature on the predicted no-effect concentration (PNEC) values. The analysis results alongside relevant PNECs are presented (Fig.2). Considering the wastewater micro-pollution characteristics, the concentrations of SC, SA, SNI, and heavy metals such as Cu exceed the NOEC parameter (Fig. 2A and B) for native species (Antarctic red alga and Antarctic sea urchin). It should be noted that this observation does not include the dilution factor after discharge.

For multivariate parameter analysis, physico-chemical data were divided into two series, i.e. with raw wastewater results included (Fig. 3 A,C) and without (Fig. 3 B,D). For this analysis the redox parameter has been excluded. In addition, in the case of data without raw wastewater (Fig. 3 B,D), in order to characterise the most important parameter among components with low concentrations (micropollution) the following variables were also removed: COD, conductivity, pH, TP, TN. For all four series of data, two principal components were identified that represent 99% (Fig.3 A), 96% (Fig. 3 B), 99% (Fig. 3 C) and 99% (Fig. 3 D) of the variance, respectively. For the first case (Fig. 3 A), PC1 and PC2 were found to have a strong correlation with COD, but correlations with Fe and conductivity for both years were also significant. On the other hand, when the COD was excluded, (Fig. 3 C) PC1 and PC2 were strongly positively correlated with Fe for both years of data. In addition, there is positive correlation with $N\text{-}NH_4^+$ for the data obtained in 2019 (II). The PCA analysis performed for the series without raw wastewater characteristic (Fig. 3 B) confirmed a positive correlation with COD and conductivity, but it is noteworthy that there is a noticeable correlation with Zn for the first year data and Fe for the second year data. Moreover, participation of the second components (PC2) in the representation of the entire variance increases significantly, up to 28%. These results are confirmed in the fourth case (Fig. 3 D), in which some of the variables were omitted.

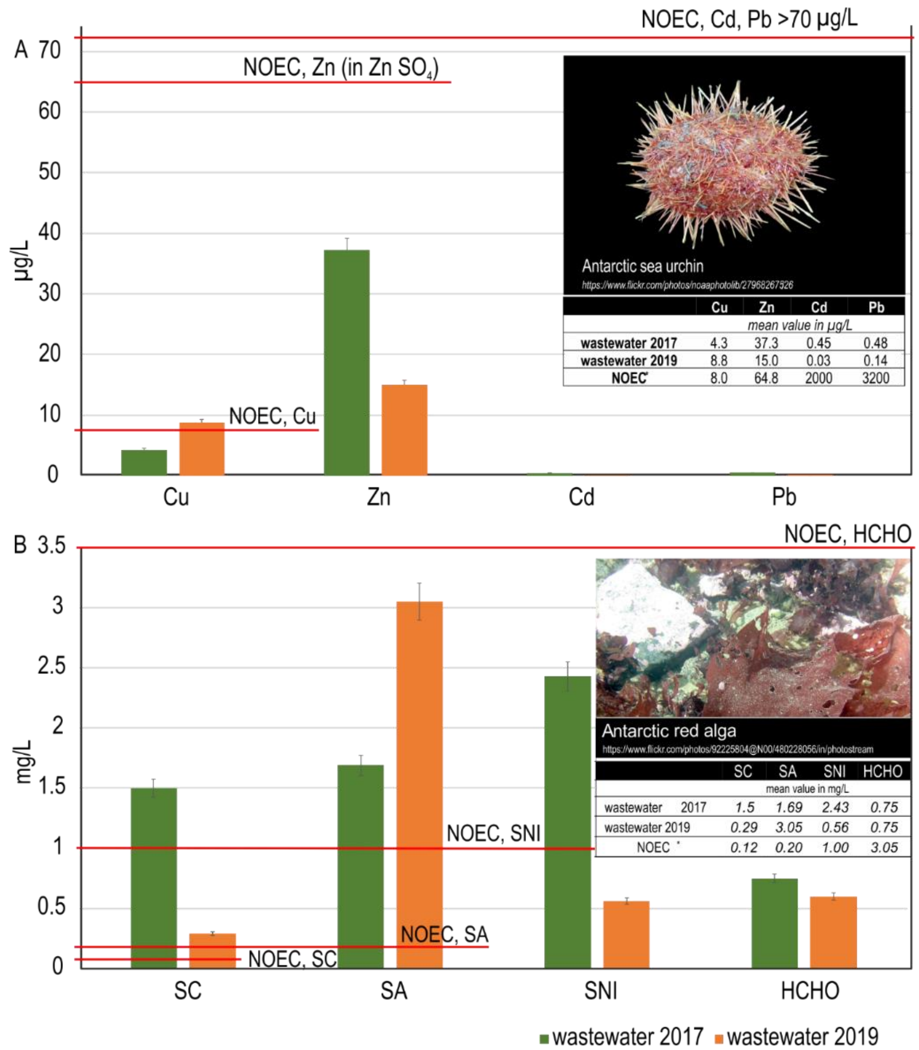

Figure 2. Selected micro-pollution concentrations in wastewater: A) heavy metals in wastewater in relation to the literature values of the no observed effect concentrations (NOECs) on Antarctic sea urchins (King and Riddle, 2001); B) organic micro-pollution concentrations in wastewater in relation to the literature values of the NOECs on Antarctic red alga (Gheorghe et al., 2013; Steber, 2007) Abbreviations: *SC – sum of cationic surfactants; SA –sum of anionic surfactants; SNI – sum of non-ionic surfactants; HCHO-formaldehyde*

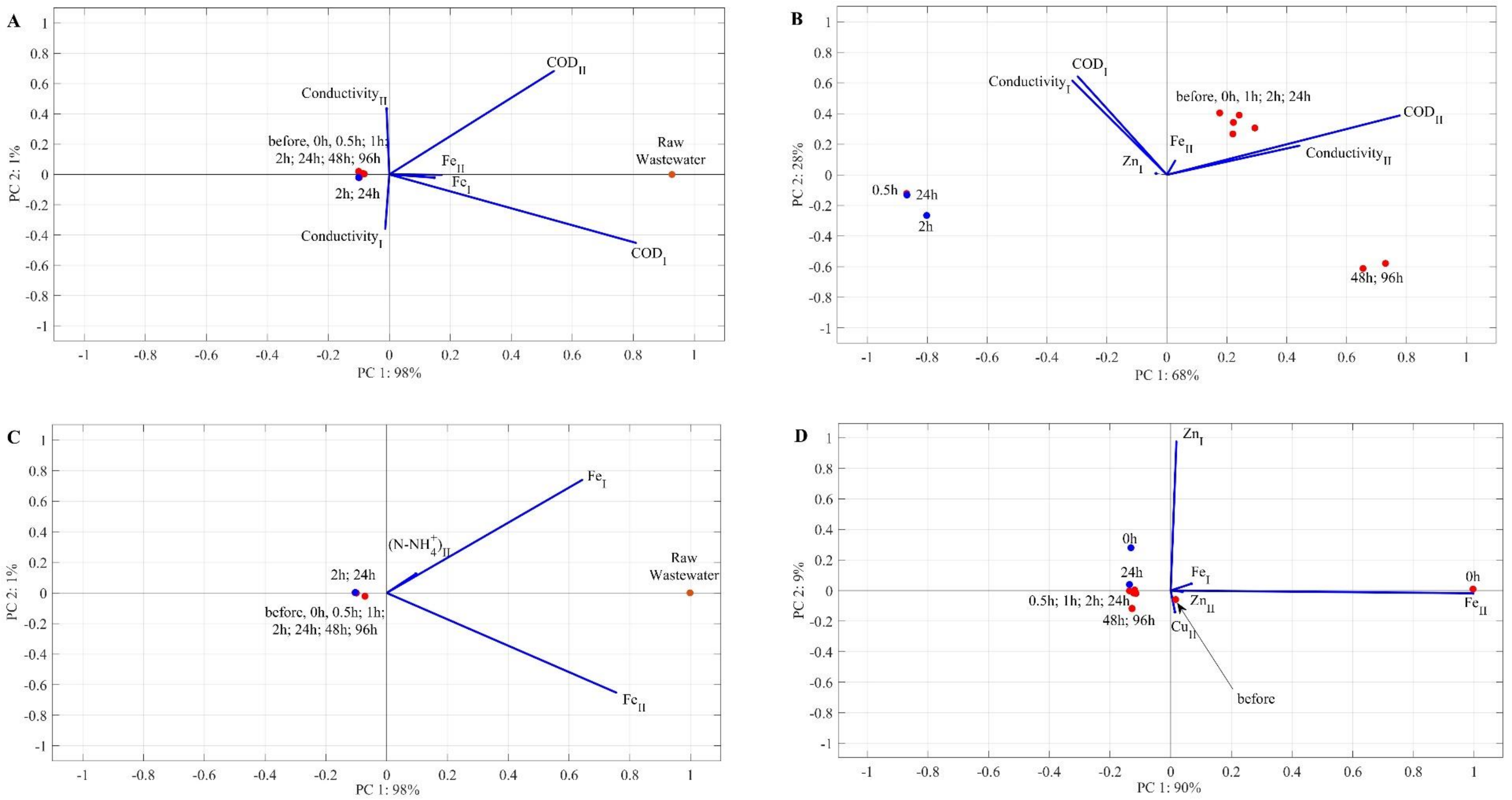

Figure 3. PCA biplots for various data sets. Projection of environmental variables and cases (sampling points) on the plane of two principal components: A. Entire data set for recipient water and raw wastewater analysis (excluding redox parameter); B. Entire data set for recipient water C. Reduced data set for recipient water and raw wastewater analysis (excluding redox parameter); D. Reduced data set for recipient water. Blue dots refer to the sampling campaign in 2017, red dots to 2019; I and II in subscript means results obtained during sampling campaign in 2017 and in 2019, respectively

4. Discussion

Wastewater generated at polar research stations is mainly derived from domestic (e.g., kitchens, toilets, laundry rooms, and bathrooms) and from some technological (laboratories, repair workshops, etc.) sources. This type of wastewater has properties typical of municipal wastewater (for details, see Table 1). Different stations, however, may generate different kinds of wastewater depending, e.g., on the specific research conducted there. In wastewater originating from Antarctic stations, organic compounds of limited biodegradability (Wild et al., 2015), including microplastics (Gheorghe et al., 2013), hydrocarbons, surface active agents and endocrine disrupting compounds (Smith and Riddle, 2009), as well as pharmaceuticals (González-Alonso et al., 2017), were noted.

Table 1. Wastewater physico-chemical parameters from Arctowski and other Antarctic stations

STATION NAME (ownership)	YEAR	TSS	COD_{total} ($COD_{dissolved}$)	BOD_5	TP	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$	TN	Ref.
		[mg/L]	[mgO_2/L]	[mgO_2/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	
Arctowski Station (Poland)	2017	-	2390 (406)	1386	3.21	11.2	1.33	0.095	42.0	(present study)
	2019	-	1618 (1019)	806	3.44	63.9	0.863	0.035	98.2	
Davis Station (Australia)	2010	668 - 1896	1444 - 4823	90 - 3167	36-158	-	-	-	214-704	(Stark et al., 2015)
McMurdo Station (USA)	1989-1992	33-540	113-1000	26-1600	1.6–250	2.1-60	<0.04-0.66	<0.003-0.04	9.3-130	(Crockett, 1997)
	1992-1993	85-1000	360-4100	170-1300	2.9-13	3.5-39	<0.04-0.36	<0.01-0.45	18-100	
Wasa Station (Sweden)	no data	1100	5800	3800	-	2.3	-	-	-	(Tarasenko, 2008)
Dome A station (China)	no data	40-60	80-120	30-50	-	5	-	-	-	(Tarasenko, 2008)

Nevertheless, the development and implementation of proper treatment methods may significantly mitigate this anthropogenic impact despite the lack of appropriate legal regulations for wastewater discharge in the requirements of the Environmental Protocol to the Antarctic Treaty (the Madrid Protocol).

4.1 Macro- and micro-pollution assessment in the western shore of Admiralty Bay

Presented experimental design lends itself to answer questions about the initial dilution and dispersion of wastewater. In this study, according to basic parameters such as COD, pH, redox and nutrients (Table S2, Supplementary Material), receiver quality returned to the same state as before wastewater discharge, in general, after 24 h. Based on this indication, it could be assumed that Arctowski Station wastewater management achieved the Protocol requirements (Annex III, Article 5) and that the receiving marine environment provided assimilative capacity, suitable dilution and rapid dispersal conditions. Nutrients are not suspected to have a significant effect on fauna and flora in the vicinity of the wastewater discharge. This is due to their rapid dilution in the waters of the Admiralty Bay, which has been demonstrated in this research. There is no eutrophication phenomenon in the vicinity of the Arctowski station, as in the case of urbanized areas. Nonetheless, natural biogeochemical cycles are potentially influenced by the continuous discharge of easily biodegradable wastewater ($BOD_5/COD \geq 0.5$). This is of special concern and should be monitored, since the yearly volume of wastewater generated by the station can reach 80.7 m^3. Considering the mean values of daily water consumption (Table S1, Supplementary Material) and measured nutrient concentrations (Table S2, Supplementary Material), based on the product of these values, the total load of nitrogen is estimated to reach 2.28 - 5.34 kg/year (0.61 - 3.48 kg/year in ammonia form), phosphorus is estimated to reach 0.18 - 0.19 kg/year (0.06-0.11 kg/year in phosphate form), and organic matter expressed as COD is estimated to reach 88.0 - 129.9 kg/year. Especially in nutrient-limited environments, any wastewater discharge entering the food web may upset the balance of the environment. High levels of organic material in wastewater may consume oxygen in water, causing reduced dissolved oxygen zone formation (Smith and Riddle, 2009). Hence, bottom water zones together with benthic invertebrates may be particularly at risk.

In our research, as important chemical markers of wastewater dissemination in the receiving environment, trace metals, surfactants and formaldehydes were chosen (Fig. S2, Table S3, Supplementary Material). Among the trace metals, potentially toxic heavy metals(Thornton et al., 2001), such as Cd, Cr, Cu, Ni, Pb and Zn, have been analysed. Moreover, taking into account ongoing discussion regarding the increase in filterable Fe concentration caused by the inflow of surface runoff into Antarctic costal seawater (Hodson et al., 2017), this element has also been analysed, considering wastewater as an additional source of Fe. Heavy metals were present in the Arctowski Station wastewater, with Zn, Pb, Fe and Ni at the highest concentrations (Table S3, Supplementary Material), and Zn and Fe of high significance (Fig. 3 C, D). Sources of Cd, Zn, Cu and Ni in domestic wastewater include personal care products, pharmaceuticals, cleaning products and liquid wastes (El Khatib et al., 2012; Eriksson and Donner, 2009; Tjandraatmadjia et al., 2006). These products used by people staying at the station go directly to the sewage tank or indirectly along with the waste. Part of the Zn and Cd load may also originate from transport emissions (El Khatib et al., 2012). Additionally, plumbing might be a source of Cu and Pb (Drozdova et al., 2019; El Khatib et al., 2012). In this case, the gradual replacement of Pb water pipes and fittings is recommended, especially during building renewal and renovation programmes (Thornton et al., 2001). Iron in wastewater may also originate from household products such as floor cleaners, laundry soakers or aerosol deodorants (Tjandraatmadjia et al., 2006). However, in the case of iron, its concentration in wastewater is also influenced by natural factors (Szopińska et al., 2018). Fresh water in periglacial environments in this area contains easily soluble Al and Fe because the environment of King George Island is rich in pyrite (Paulo and Rubinowski, 1987). Considering the noticeable increase in Zn and Fe concentrations in seawater after wastewater discharge (Table S2, Supplementary Material, Fig. 3C and D), their accumulation in the impacted sediments is expected (Goldberg et al., 1975). Future studies are needed to analyse the responses of marine biota and benthic communities to the presence of heavy metals since their toxic effects have already been indicated (Bryan and Langston, 1992; King and Riddle, 2001; Lenihan et al., 2003; Sfiligoj, 2013).

Another special group of micropollutants analysed in this study are surfactants. Currently, surfactants are common components of the reagents used in industries and households (washing, wetting, emulsifying, and dispersing) due to their specific properties. As a result, different types of surfactants are added *inter alia* to personal care products, laundry and cleaning detergents (Olkowska et al., 2012). Thus, these compounds ultimately end up in wastewater. The classification of surfactants is usually made based on the chemical characteristics of hydrophobic groups: (1) ionic: cationic (e.g., benzyl ammonium chloride and dialkyl dimethyl ammonium chloride) and anionic (e.g., linear alkylbenzenesulfonates, secondary alkyl sulfates, perfluorooctanoic acid, and perfluorooctane sulfonates); (2) non-ionic: (e.g., octylphenol, nonyl phenol ethoxylates, and octylphenol ethoxylate) (Olkowska et al., 2012). In this study, the concentrations of cationic, anionic and non-ionic surfactants were analysed by spectrophotometry. This method is very useful for regular monitoring of this group of compounds and could be applied to Arctowski Station due to its reliability, availability and ease of use, which are important in the case of a lack of qualified staff (analytical chemists), especially during winter. The obtained results show the highest concentrations of anionic and non-ionic surfactants in both wastewater and seawater (Fig. S2, Supplementary Material). This finding is consistent with the more frequent use of anionic and non-ionic surfactants than cationic surfactants (Olkowska et al., 2015).

We also checked the formaldehyde concentration level, which was detectable in wastewater and in seawater only directly after discharge (0.04-0.08 mg/L). Due to its high reactivity, colourless nature, stability and low cost, formaldehyde has been applied as a resinification agent, curing agent, synthetic agent, disinfectant, fungicide, and preservative (Lotfy and Rashed, 2002). Considering its minor concentration in the studied wastewater samples (0.60 - 0.75 mg/L), formaldehyde may originate from agents and disinfectants used during everyday activities at the station. Nevertheless, this aldehyde is highly toxic to living organisms – it may inhibit the physiological activity of cells by creating permanent connections with amino groups of proteins. Due to the ability to damage DNA and cause mutations in microorganisms, it also creates a carcinogenic risk. Hence, any wastewater containing formaldehyde might be toxic to microorganisms (Kowalik, 2011). Note that in niches exposed to formaldehyde or surfactants and other biocides (which permeabilize cell membranes and act as disinfectants), bacteria have evolved detoxification systems, e.g., the *frm*RA(B) operon (Denby et al., 2016) or *qac*E efflux pump genes (Pal et al., 2015).

Considering the available water consumption data (Table S1, Supplementary Material), the total annual loads of surfactants (SC, SA, SNI) and formaldehyde are estimated to be 0.016 - 0.082; 0.092 - 0.165; 0.030 - 0.132 and 0.032 - 0.041 kg/year, respectively. Because wastewater is constantly disposed into Admiralty Bay, it may influence indigenous species. Potential environmental impacts, expressed as NOEC (the highest concentration/dose of a given substance in the test organism that does not cause severe effects or a significant increase), are presented in relation to micro-pollution detected in wastewater. The data summarised in Fig. 2 do not take into account the dilution factor that occurs in seawater after discharge. Therefore, it is merely illustrative to present the potential risks of raw sewage emissions to the environment. The SC, SA, SNI, and Cu concentrations exceed the NOEC parameter, which suggests that these substances may cause damage in the tested species (*Antarctic red alga* and *Antarctic sea urchin*). Moreover, metal toxicity is also known for other species, e.g. two Antarctic marine microalgae – *Phaeocystis antarctica* (Gissi et al., 2015) and *Cryothecomonas armigera* (Koppel et al., 2017). However, data are presented via different toxicity assays to NOEC. These two species represent a very sensitive and a more tolerant species to metal contaminants, respectively. Based on 10% inhibition of population growth rate (IC10) values, *Phaeocystis antarctica* was most sensitive to copper (3.3 mg/L), followed by cadmium (135 mg/L), lead (260 mg/L), and zinc (450 mg/L) (Gissi et al., 2015). On the other hand, for marine microalga *Cryothecomonas armigera*, the concentrations that reduced population growth rate by 10% (EC10) after 24-day for Cu, Pb, Zn, Cd and Ni were 21.6, 152, 366, 454, and 1220 mg/L^{-1} , respectively. Moreover, recently the data for the sea urchin used in Fig. 2 was reanalysed in (Koppel et al., 2020) to give EC values. The investigation showed EC10 and EC50 values, respectively, of Cu: 0.9 and 1.4 $\mu g/L^{-1}$, and Zn: 56 ± 31 and 195 ± 44 $\mu g/L^{-1}$ for 23 day larval development inhibition. Hence based on data presented by Koppel and co-authors (Koppel et al., 2020) processed considering the risk of contaminant mixtures using a toxic-units approach, the combination of Cu and Zn concentrations in the 2017 wastewater (Fig. 2) may be considered harmful *inter alia* to the sea urchin (e.g. *S. neumayeri*). Additionally, preliminary studies for microalgae have shown that *P. antarctica* and *C. armigera* are capable of accumulating potentially toxic concentrations of metals like copper and zinc (Koppel et al., 2020).

Moreover, as previously mentioned, trace metals have an affinity for particulate organic matter and thus may accumulate in the bottom zone (Licínio et al., 2008). Hence, a detailed study of micro-pollution concentration levels in sediments and their environmental (ecotoxicological) impact needs to be addressed as a next step in research on wastewater disposal influence on wildlife health in Admiralty Bay.

4.3 Wastewater technology innovations for sustainable impacts of Arctowski Station

The treatment of domestic wastewater is a multistep process that includes physical, biological and chemical treatment steps (USEPA, 2012). Recently, advanced treatment methods such as advanced oxidation processes e.g. ozonation, or sorption-based procesess e.g. activated carbon technologies (Kosek et al., 2020)_have been applied consecutively in the context of pharmaceutical and other organic micro-pollution removal. According to the obtained results, there is no doubt that proper wastewater treatment is required to limit the adverse impact on receiving water and to comply with environmental safety requirements. However, the choice of proper wastewater treatment method/s is a complex engineering and economic problem that depends on the properties and volumes of generated wastewater, expected discharge requirements, potential sludge management and local conditions.

In the case of wastewater treatment plant construction in Antarctica, it is necessary to consider at least (1) operations at low temperatures (even -60°C); (2) large fluctuations in station population between the summer and winter seasons, causing significant variations in the generated wastewater volume; and (3) different effluent characteristics within the stations. Operations at low temperatures require heating or insulation of the wastewater lines, holding tanks, pumps and other treatment facilities (Stark et al., 2015). Moreover, the majority of wastewater treatment technology requires adequate pipe heating systems to prevent freezing and needs to be placed in enclosed buildings to limit the possibility of contact with wildlife. Additionally, the differences in wastewater characteristics are noticeable between various bases (Table 1).

As an example, we may consider BOD values in the non-treated wastewater, which in Antarctica are relatively high (up to 3167 mg/L at Davis Station (Stark et al., 2015)) and associated with high calorific value food input that is rich in fat within the standard diet (Connor, 2008). In addition to organic matter, conventional wastewater treatment plants are designed to remove nutrients and suspended solids. Nitrogen can be removed from wastewater mainly during biological processes, while phosphorus is removed mostly by biological treatment or by chemical precipitation (with iron or aluminium salts). However, in polar regions, treatment effectiveness due to extreme temperature conditions may vary significantly. Thus, the implementation of advanced wastewater treatment is needed, especially in terms of micro-pollution contamination. According to the available survey, in the majority of Antarctic stations, there is a lack of wastewater treatment. Gröndahl and co-authors (Gröndahl et al., 2009) reported that 37% of permanent stations and 69% of summer Antarctic stations lack any form of treatment facility. However, apart from biological and secondary treatment, even the presence of septic tanks or maceration is considered wastewater treatment (Gröndahl et al., 2009). Nevertheless, in recent years, ozonation, micro/ultra/nanofiltration, biologically activated carbon filtration, reverse osmosis, ultraviolet disinfection and chlorination were tested to obtain potable water and nontoxic brine concentrate in Antarctica (Allinson et al., 2018), especially for the separated 'grey' wastewater (liquid waste without input from toilets). This shows the efforts being made to minimise the environmental impact caused by wastewater effluent disposal. Considering the high expectation for protecting the Antarctic environment, novel approaches should also be considered, including the zero discharge of contaminants or introduced microorganisms, as well as the potential reuse of treated water, which is an important aspect of circular economy (Stark et al., 2015). The choice of technology should consider efficient energy consumption and reduction of carbon footprint (Zaborowska et al., 2019). There are some innovative technologies based on advanced oxidation processes that may also be considered for implementation in polar regions or in small remote communities. Currently, electrolysis is a promising technology for small and variable flow wastewater treatment installations where simplicity of use, with high efficiency of removal of micropollutants and reduction in by-products, is important (Gomez-Ruiz et al., 2017). Electrochemical experiments were conducted with anodes consisting of boron-doped diamond (BDD) during landfill leachate treatment, which is very hard to treat. It was found that in BDD, organic substances were preferentially oxidised via a fast reaction with hydroxyl radicals, leading to very high removal rates, including micropollutants like bisphenol A (BPA), perfluoroalkyl and polyfluoroalkyl substances (PFASs) etc. (Fudala-Ksiazek et al., 2018; Gomez-Ruiz et al., 2017, Pierpaoli et al., 2021). BDD-based electrochemical oxidation could also be integrated with biochemical treatment processes to obtain synergistic effects in pollutant degradation. Zhao and co-authors (Zhao et al., 2010) used a synergistic combination of biochemical treatment and electrochemical oxidation for the selection treatment of landfill leachate on the electrode. Therefore, technology that combines BDD with a biological membrane reactor enables the effective removal of ammonium nitrogen and organic matter (together with micropollutants and microorganisms), and the treatment efficiency is rather stable and high, despite the high flow variability of wastewater. An additional advantage is the limited production of excess sludge (Fudala-Ksiazek et al., 2018). Thus, such a module system seems to be the optimal solution for wastewater treatment in the Antarctic region.

5. Conclusions

Specific properties of wastewater generated at polar research stations may have direct consequences on the Antarctic ecosystem. This study shows that Arctowski Station wastewater contains contamination such as trace metals, different groups of surfactants and formaldehydes.

Parameters such as the SC, SA and SNI surfactants may be selected as markers of human activity in Antarctica and can be considered as parameters for routine wastewater quality control before its disposal into the environment. Moreover, our results also indicate that wastewater contamination cannot be measured in seawater after one day of natural processes, except for the presence of anionic surfactants and Zn. Nevertheless, these results indicate that Arctowski Station wastewater management achieved the Protocol requirements (Annex III, Article 5) and that the receiving marine environment provided assimilative capacity, suitable dilution and rapid dispersal conditions. However, the Protocol does not include microbiological parameters and emerging pollutants such as BPA and PFAS. Detailed examination of the wide range of micropollution determination (including pharmaceuticals, poly- and per-fluorinated compounds, pesticides etc.) is needed to fully assess wastewater pollution and its impact on Antarctic ecosystems. Such detailed knowledge will help to focus appropriate research in the future and to target proper prevention and mitigation actions, especially in the development of suitable wastewater treatment systems in Antarctica to reduce its negative impact. In this process, in addition to scientific stations, the potential impact of increasing commercial tourism must also be considered. .

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8. Supplementary Material

Supplementary Material consists of: S1. Additional information regarding the influence of wastewater discharge in Admiralty Bay, and S2. Detailed information regarding the applied chemical methods.

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Supplementary Material to

First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica)

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S1. Additional information regarding the influence of wastewater discharge in Admiralty Bay

Table S1. Detailed data regarding water consumption and the number of people in recent years at Arctowski Station.

	daily water consumption [L]			**number of people at the station**		
	mean	*max*	*min*	*mean*	*max*	*min*
2016	153	193	117	14	26	8
2017	138	181	86	16	37	8
2018	152	221	111	13	25	6
2019	153	180	111	16	33	8
mean	149	194	106	15	30	8

Table S2. Basic chemical analysis results in wastewater and marine water samples.

PARAMETER	YEAR	RAW WASTEWATER	SEAWATER SAMPLING TIME REFERRING TO THE DISCHARGE TIME									
			sampling point no 1								*sampling point no 2*	
			before	*0 h*	*0.5 h*	*1 h*	*2 h*	*24 h*	*48 h*	*96h*	*2h*	*24 h*
pH [-]	2017	6.88	8.2	8.1	8.08	8.11	8.11	8.18	-	-	8.17	8.16
	2019	7.63	7.36	7.21	-	7.34	7.22	7.24	7.28	7.29	-	-
Conductivity [mS/cm]	2017	1.478	47.8	43.8	53.4	57.8	46.7	58.7	-	-	45	60.2
	2019	1.737	36.7	34.3	-	36.4	47.3	48.3	47.4	37.6	-	-
Redox [mV]	2017	119.8	119.8	120.5	119.5	119.1	118.7	117.7	-	-	118.4	117.4
	2019	152.5	85.6	10.7	-	39.6	47.4	49.6	61.2	70.1	-	-
COD [mgO_2/L]	2017	2390 (diss. 406)	50.3	58.6	57.6	55.1	52.3	50.5	-	-	49.7	50.0
	2019	1618 (diss. 1019)	73.0	75.4	-	75.2	74.2	73.0	74.5	73.2	-	-
P-PO_4^{3-} [mg/L]	2017	1.12	0.053	0.072	0.059	0.049	0.052	0.055	-	-	0.053	0.058
	2019	2.09	0.069	0.120	-	0.073	0.064	0.059	0.068	0.070	-	-
TP [mg/L]	2017	3.21	0.921	2.10	0.950	0.820	0.850	0.890	-	-	0.085	0.091
	2019	3.44	0.991	1.91	-	0.925	0.825	1.20	0.853	0.655	-	-
N-NH_4^+ [mg/L]	2017	11.2	<0.015	0.078	0.031	0.068	0.029	0.052	-	-	0.047	0.035
	2019	63.9	0.03	0.06	-	0.04	0.11	0.10	0.06	0.05	-	-

Table S2. C.D.

$N\text{-}NO_3^-$ [mg/L]	2017	1.33	0.126	0.148	0.131	0.126	0.125	0.104	-	-	0.074	0.076
	2019	0.863	0.103	0.128	-	0.112	0.109	0.108	0.106	0.098	-	-
$N\text{-}NO_2^-$ [mg/L]	2017	0.095	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	-	-	<0.015	<0.015
	2019	0.035	<0.015	<0.015	-	<0.015	<0.015	<0.015	<0.015	<0.015	-	-
TN	2017	42	0.228	0.312	0.254	0.225	0.213	0.197	-	-	0.179	0.172
[mg/L]	2019	98.2	0.315	1.21	-	0.384	0.239	0.189	0.062	<LOD	-	-

Table S3. Influence of wastewater discharge on marine water chemical characteristics in terms of selected heavy metal concentrations in the vicinity of Arctowski Station, Admiralty Bay

HEAVY METALS [µg/L]	YEAR	RAW WASTEWATER	SEAWATER SAMPLING TIME REFERRING TO THE DISCHARGE TIME									
			sampling point no 1								*sampling point no 2*	
			before	*0 h*	*0.5 h*	*1 h*	*2 h*	*24 h*	*48 h*	*96h*	*2h*	*24 h*
Cr	2017	4.43	0.31	0.34	0.42	0.43	0.38	0.33	-	-	0.35	0.32
	2019	2.67	0.53	0.59	-	0.68	0.64	0.55	0.57	0.79	-	-
Co	2017	1.68	0.02	0.01	0.01	0.01	0.02	0.01	-	-	0.01	0.01
	2019	2.13	0.06	0.14	-	0.03	0.02	0.02	0.02	0.02	-	-
Ni	2017	23.26	0.83	0.61	0.91	0.95	0.64	0.77	-	-	0.55	0.99
	2019	9.06	0.22	0.31	-	0.21	0.28	0.28	0.28	0.33	-	-
Cu	2017	4.27	0.17	0.11	0.17	0.20	0.17	0.10	-	-	0.12	0.09
	2019	8.80	0.53	0.86	-	0.25	0.53	0.89	1.14	1.41	-	-
Zn	2017	37.29	1.16	3.04	2.13	1.94	2.52	2.1	-	-	8.42	3.08
	2019	15.02	0.19	0.98	-	0.21	0.05	0.04	0.06	0.04	-	-
Cd	2017	0.45	0.02	0.01	0.01	0.02	0.01	0.01	-	-	0.01	0.02
	2019	0.03	0.02	0.02	-	0.01	0.01	0.01	0.01	0.01	-	-
Fe	2017	428	0.54	2.01	0.53	0.69	0.48	0.39	-	-	0.44	0.42
	2019	504	3.31	24.42	-	0.43	0.34	0.28	0.24	0.24	-	-
Pb	2017	0.48	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	-	<0.01	<0.01
	2019	0.14	<0.01	<0.01	-	<0.01	<0.01	<0.01	<0.01	<0.01	-	-

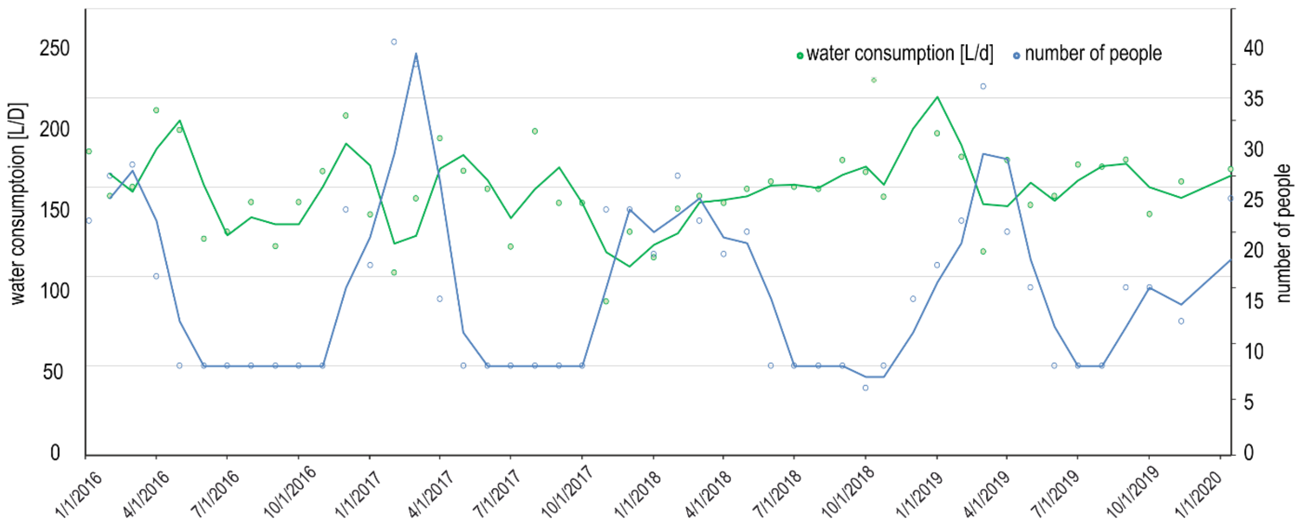

Figure S1. Water consumption in relation to the number of people present at Arctowski Station between Nov 2014 and Jan 2019. Data are obtained from Arctowski Station. Moving-average (period 2) line chart (for both: water consumption – green line, and no. of people – blue line) is applied.

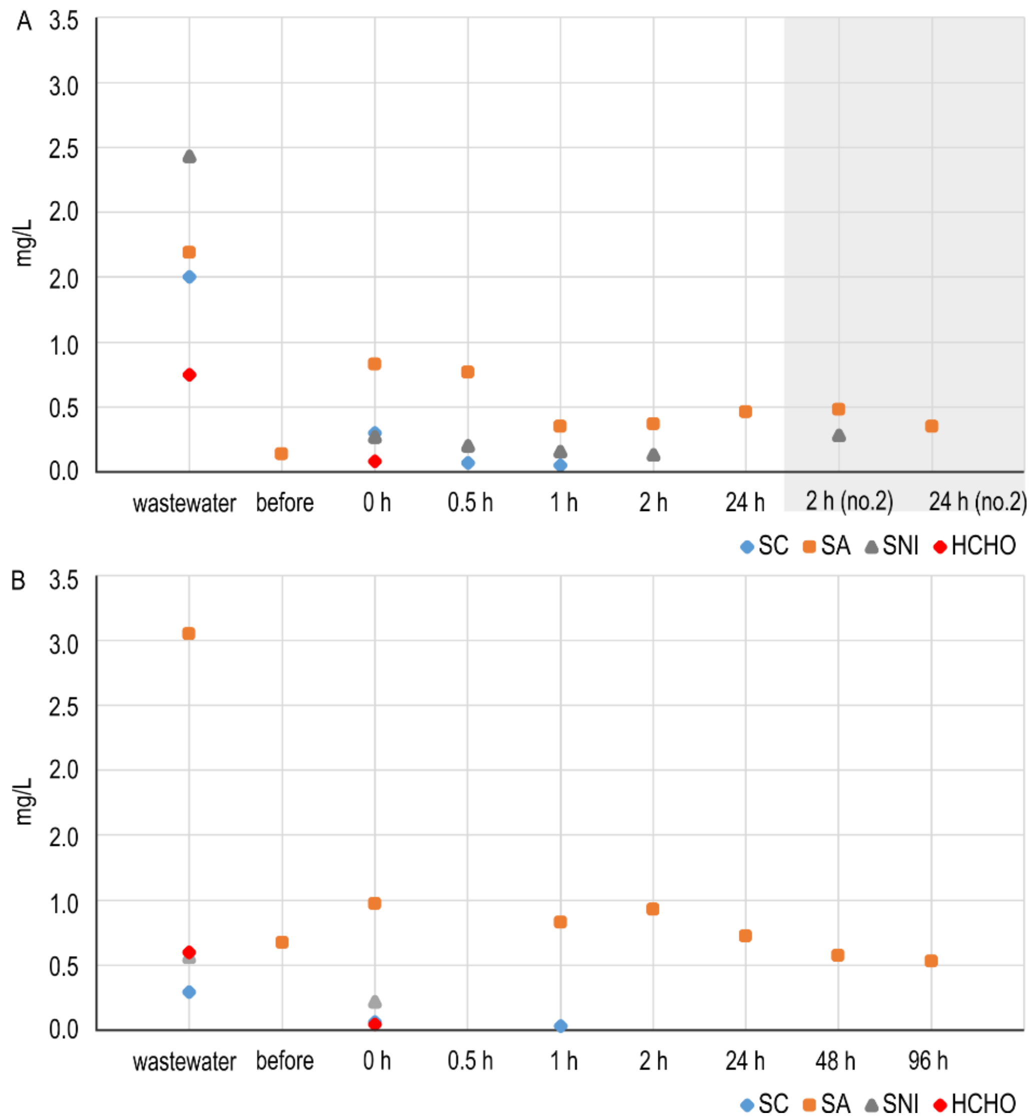

Figure S2. Dilution of wastewater in Admiralty Bay at the discharge point at Arctowski Station: A) 2017 and B) 2019. Abbreviations and descriptions: SC- sum of cationic surfactants; SA- sum of anionic surfactants; SNI- sum of non-ionic surfactants; HCHO- formaldehyde; white area – sampling point no. 1; grey area – sampling point no. 2. The error bars for each data point have been omitted to increase the readability of the chart. Data not shown on graph means that concentration are <LOD (applies to all the time series data where there are no points for SC, SNI or formaldehyde, except 0.5 h in B, where was no measurements).

S2. Detailed information regarding the applied chemical methods

Table S4. Basic analytical parameters characterising the applied methods.

PARAMETER/ANALYTE	TEST NAME AND CONCENTRATION RANGE / EQUIPMENT	COMPANY	LOD	LOQ	MEASUREMENT RANGE	CONFIDENCE INTERVAL (cuvette tests)	CONFIDENCE INTERVAL (electronic multimeters)
pH	HL–HQ40d Multimeter	Hach Lange	-	-	0 – 14	-	±0.002
Redox	HL–HQ40d Multimeter	Hach Lange	-	-	-1500 – +1500 mV	-	±0.1 mV
Conductivity	HL–HQ40d Multimeter	Hach Lange	-	-	0.01 µS/cm – 400 mS/cm	-	± 0.5 %
COD, chemical oxygen demand	LCK 1414 5–60 mg/L	Hach Lange	0.6 mg/L	2.0 mg/L	5.0 – 60 mg/L O_2	± 0.75 mg/L	
$P\text{-}PO_4^{3-}$	LCK 349 0.05–1.5 mg/L	Hach Lange	0.007 mg/L	0.020 mg/L	0.05 – 1.5 mg/L	± 0.010 mg/L	
TP, total phosphorus	LCK 349 0.05–1.5 mg/L	Hach Lange	0.007 mg/L	0.020 mg/L	0.15 – 4.5 mg/L	± 0.010 mg/L	
$N\text{-}NH_4^+$	LCK 304, 0.015–2.0 mg/L NH_4^+–N	Hach Lange	0.005 mg/L	0.015 mg/L	0.015 – 2.0 mg/L	± 0.012 mg/L	
$N\text{-}NO_3^-$	LCK 339 0.23–13.50 mg/L NO_3^-–N	Hach Lange	0.210 mg/L	0.629 mg/L	0.23 – 13.5 mg/L	± 0.45 mg/L	
$N\text{-}NO_2^-$	LCK 341, 0.015–0.6 mg/L NO_2^-–N	Hach Lange	0.012 mg/L	0.037 mg/L	0.015 – 0.6 mg/L	± 0.035 mg/L	
TN, Total nitrogen	Laton Total Nitrogen cuvette test 1–16 mg/L	Hach Lange	0.116 mg/L	0.350 mg/L	1 – 16 mg/L	± 0.229 mg/L	

Table S4 C.D.

<table>
<tr><td>BOD, Biological oxygen demand</td><td>OxiTop, OC 100</td><td>WTW</td><td>-</td><td>-</td><td>0 – 4000 mg/L</td><td></td><td>± 1 %</td></tr>
<tr><td>sum of cationic surfactants</td><td>0.05–1.50 mg/L</td><td>Spectroquant, Merck</td><td>0.027 mg/L</td><td>0.05 mg/L</td><td>0.05 – 1.50 mg/L</td><td>± 0.017 mg/L</td><td></td></tr>
<tr><td>sum of anionic surfactants</td><td>0.05–2.0 mg/L</td><td>Spectroquant, Merck</td><td>0.030 mg/L</td><td>0.05 mg/L</td><td>0.05 – 2.00 mg/L SDSA (calculated as sodium 1-dodecanesulfonate)</td><td>± 0.10 mg/L</td><td></td></tr>
<tr><td>sum of non-ionic surfactants</td><td>0.1–7.5 mg/L</td><td>Spectroquant, Merck</td><td>0.062 mg/L</td><td>0.15 mg/L</td><td>0.1 – 7.5 mg/L</td><td>± 0.075 mg/L</td><td></td></tr>
<tr><td>HCHO-formaldehyde</td><td>No. 14678,
0.02–8 mg/L</td><td>Spectroquant, Merck</td><td>0.040 mg/L</td><td>0.10 mg/L</td><td>0.10 – 8.00 mg/L</td><td>± 0.087 mg/L</td><td></td></tr>
<tr><td>Cr</td><td rowspan="8">ICP-MS</td><td rowspan="8">ICP-MS X Series 2 Thermo Scientific</td><td rowspan="5">0.030 µg/L</td><td rowspan="5">0.10 µg/L</td><td rowspan="5">0.10–
1000 µg/L</td><td rowspan="5">-</td><td rowspan="5">0.5-1.5%*</td></tr>
<tr><td>Co</td></tr>
<tr><td>Ni</td></tr>
<tr><td>Cu</td></tr>
<tr><td>Zn</td></tr>
<tr><td>Cd</td><td>0.002 µg/L</td><td>0.006 µg/L</td><td>0.01–1000 µg/L</td><td>-</td><td>0.5-1.5%*</td></tr>
<tr><td>Pb</td><td>0.003 µg/L</td><td>0.01 µg/L</td><td>0.01–1000 µg/L</td><td>-</td><td>0.5-1.5%*</td></tr>
<tr><td>Fe</td><td>0.30 µg/L</td><td>0.60 µg/L</td><td>0.60–
1000 µg/L</td><td>-</td><td>0.5-1.5%*</td></tr>
</table>

* relative standard deviation