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FACULTY OF CHEMISTRY

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Supervisor *Signature*	Auxiliary supervisor *Signature*
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Gdańsk, 2022

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"Nauka jest jak niezmierne morze ... Im więcej jej pijesz, tym bardziej jesteś spragniony."

Stefan Żeromski, Syzyfowe prace

"Dziś, bardziej niż kiedykolwiek, nauka wydaje się kluczem do przetrwania. Zarówno dla naszej planety, jak i nas samych jako narodu oraz naszego dobrobytu i bezpieczeństwa. Nadszedł czas, byśmy znowu naukę zaczęli traktować jako jedną z najważniejszych dziedzin życia."

Barack Obama

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List of publications constituting the basis of the dissertation

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II. **Joanna Potapowicz**, Dimitra Lambropoulou, Christina Nannou, Krystyna Kozioł, Żaneta Polkowska, Occurrences, sources, and transport of organochlorine pesticides in the aquatic environment of Antarctica, *Sci. Total Environ.*, 725, 139475, 2020, doi 10.1016/j.scitotenv.2020.139475 (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.

III. **Joanna Potapowicz**, Danuta Szumińska, Małgorzata Szopińska, Sebastian Czapiewski, Żaneta Polkowska, Electrical conductivity and pH in surface water as tool for identification of chemical diversity, *Ecol. Chem. Eng., S*, 27, 95-111, 2020, doi 10.2478/eces-2020-0006, (IF: 1.545; 5-Year IF: 1.504; 40 pt), Q3.

IV. **Joanna Potapowicz**, Danuta Szumińska, Małgorzata Szopińska, Robert Józef Bialik, Katarzyna Machowiak, Stanisław Chmiel, Żaneta Polkowska, Seashore sediment and water chemistry at the Admiralty Bay (King George Island, Maritime Antarctica) – geochemical analysis and correlations between the concentrations of chemical species, *Mar. Pollut. Bull.*, 152, 110888, 2020, doi 10.1016/j.marpolbul.2020.110888 (IF: 5.553; 5-Year IF: 5.907; 100 pt), Q1.

V. **Joanna Potapowicz**, Małgorzata Szopińska, Danuta Szumińska, Robert Józef Bialik Żaneta Polkowska, Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 1: Sediment and water analysis for PAH sources evaluation in the vicinity of Arctowski station, *Chemosphere*, 288, 132637, 2022, doi 10.1016/j.chemosphere.2021.132637, (IF: 7.086; 5-Year IF: 6.956; 140 pt), Q1.

VI. Danuta Szumińska, **Joanna Potapowicz**, Małgorzata Szopińska, Sebastian Czapiewski, Ulrike Falk, Marcin Frankowski, Żaneta Polkowska, Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 2: Organic and inorganic chemicals in snow cover at the Warszawa Icefield, *Sci. Total Environ.*, 796, 149054, 2021, doi 10.1016/j.scitotenv.2021.149054, (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.

Supporting publications

VII. Małgorzata Szopińska, Aneta Łuczkiewicz, Katarzyna Jankowska, Sylwia Fudala-Książek, **Joanna Potapowicz**, Agnieszka Kalinowska, Robert Józef Bialik, Stanisław Chmiel, Żaneta Polkowska, First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica), *Sci. Total Environ.*, 789, 147912, 2021, doi 10.1016/j.scitotenv.2021.147912, (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.

VIII. Małgorzata Szopińska, **Joanna Potapowicz**, Katarzyna Jankowska, Aneta Łuczkiewicz, Ola Svahn, Erland Björklund, Christina Nannou, Dimitra Lambropoulou, Żaneta Polkowska, Pharmaceuticals and other contaminants of emerging concern in Admiralty Bay as a result of untreated wastewater discharge: Status and possible environmental consequences, *Sci. Total Environ.*, 835, 155400, 2022, doi 10.1016/j.scitotenv.2022.155400, (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.

List of scientific expeditions

The table contains information on polar expeditions in which the author of the dissertation took part and during which the research material needed to prepare this dissertation was obtained.

Date of polar expedition	Name of polar expedition (project title)
2016/17*	Polar Expedition carried out as part of an agreement between the Institute of Biochemistry and Biophysics, Polish Academy of Science (IBB, PAS) and Gdańsk University of Technology; "Identification and determination of concentration levels and translocation of atmospheric pollutants in water reservoirs as an indicator of the adaptability of the Antarctic environment". In 2017: XLI Polar Expedition of the Institute of Biochemistry and Biophysics and Polar Expedition of scientists from the Gdańsk University of Technology. In 2018: XLII Polar Expedition of the Institute of Biochemistry and Biophysics.
2017/18*	
2018 (07.09–01.10)**	Polar Expedition as part of a grant project financed by the National Science Centre (2017/25/N/NZ9/01506); Hornsund, Polish Polar Station; "Determination of nutrients that are the primary factor in enabling growth bacteriocenosis in the Southwest Arctic River catchment Spitsbergen".
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2019 (17.01–17.04)*** and *	Polar Expedition organised partly thanks to funding by the European Union Funds as a part of the project "Development of an interdisciplinary doctoral study program with an international dimension" (POWR.03.02.00-IP.08-00-DOK/16).
2021–22 (15.11.2021–14.02.2022)***	Polar Expedition as part of a grant project financed by the National Science Centre (2020/37/N/ST10/02199); King George Island, Polish Antarctic Station; "Determination and characteristics of pollution melting due to climate change from glaciers and snow in Antarctica".

* research expeditions during which the necessary research material was obtained to prepare this dissertation
** research expeditions in which the author of the dissertation participated
*** research expeditions in which the author of the dissertation was the expedition leader

List of abbreviations and acronyms

ARG	–	antibiotic resistance genes
ASMA 1	–	Antarctic Specially Managed Area no. 1
ASPA 128	–	Antarctic Specially Protected Area no. 128
COD	–	chemical oxygen demand
DDT	–	dichlorodiphenyltrichloroethane
ECs	–	emerging contaminants
GC-MS/MS	–	gas chromatography tandem mass spectrometry
GOSEAC	–	Group of Specialists on Environmental Affairs and Conservation
HCB	–	hexachlorobenzene
HCH	–	hexachlorocyclohexane
H-ESI	–	heated electrospray ionisation source
IC	–	ion chromatography
ICP-MS	–	inductively coupled plasma – mass spectrometry
LOD	–	limit of detection
LOQ	–	limit of quantification
LRAT	–	long-range atmospheric transport
NOEC	–	no observed effect concentration
OCPs	–	organochlorine pesticides
PAHs	–	polycyclic aromatic hydrocarbons
PCA	–	principal component analysis
PCBs	–	polychlorinated biphenyls
POPs	–	persistent organic pollutants
PPCPs	–	pharmaceuticals and personal care products
RQ	–	risk quotients
SA	–	sum of anionic surfactants
SC	–	sum of cationic surfactants
SCAR	–	Scientific Committee on Antarctic Research
SEC	–	specific electrical conductivity
SNI	–	sum of non-ionic surfactants
TN	–	total nitrogen
TOC	–	total organic carbon
TP	–	total phosphorus
UHPLC-HRMS	–	ultra-high performance liquid chromatography coupled to high resolution mass spectrometry
UPLC-MS/MS	–	ultra-high performance liquid chromatography tandem mass spectrometry
UNEP	–	United Nations Environmental Program
UV-Vis	–	ultraviolet–visible spectrophotometry
QSM	–	Quaternary Solvent Manager

1. Abstract in Polish

W ramach pracy doktorskiej dokonano przeglądu literatury naukowej, którego rezultatem był wybór obszaru badawczego, rodzaju próbek oraz indywiduów chemicznych, które zostały oznaczone. Opublikowany cykl artykułów zawiera wnikliwy opis wyników analiz chemicznych próbek wód powierzchniowych, osadów i śniegu pochodzących z Szczególnie Zarządzanego Obszaru Antarktyki (ASMA 1) – Wyspy Króla Jerzego. Ponadto przeprowadzono badania dotyczące oceny wpływu zrzutu ścieków nieoczyszczonych do Zatoki Admiralicji na środowisko antarktyczne.

Celem pracy doktorskiej była analiza wyników szerokiego zakresu oznaczeń indywiduów chemicznych, obejmujących nowo pojawiające się zanieczyszczenia w wybranych środowiskach Antarktyki. Przedstawiono informacje dotyczące poziomów stężeń m.in. związków z grupy wielopierścieniowych węglowodorów aromatycznych, farmaceutyków, wybranych metali, niemetali i jonów obecnych w próbkach środowiskowych pochodzących z obszaru Antarktyki Zachodniej, źródeł pochodzenia badanych indywiduów chemicznych oraz potencjalne skutki ich obecności dla ekosystemów antarktycznych. Analiza i interpretacja wyników stanowiła podstawę do oceny losu środowiskowego oznaczanych zanieczyszczeń uwzględniając wpływ człowieka na badanym obszarze.

Zebrane dane mogą stanowić podstawę do stwierdzenia, że zanieczyszczenia obecne na tym obszarze mogą przyczyniać się do stopniowej degradacji ekosystemu Antarktyki. Ponadto stanowią podstawę do dyskusji na temat zaostrzenia przepisów prawnych dotyczących ochrony środowiska antarktycznego.

2. Abstract in English

The doctoral dissertation included a review of the scientific literature that resulted in the selection of the research area, type of samples and chemical species that were marked. The published series of articles contains an in-depth description of the results of chemical analyses of surface water, sediment and snow samples from the Antarctic Specially Managed Area (ASMA 1) – King George Island. In addition, studies have been conducted to assess the impact that raw wastewater discharge into Admiralty Bay has had on the Antarctic environment.

The aim of the doctoral thesis was to analyse the results of a wide range of determinations of chemical individuals, including newly emerging pollutants in selected Antarctic environments. Information was provided on the concentration levels of, *inter alia*, polycyclic aromatic hydrocarbon compounds, pharmaceuticals, selected metals, non-metals and ions present in environmental samples from West Antarctica, sources of origin of the studied chemical species and their potential effects on Antarctic ecosystems. The analysis and interpretation of the results was the basis for the assessment of the environmental fate of the determined pollutants, taking into account the human impact in the studied area.

The collected data may be the basis for the conclusion that the pollution present in this area may contribute to the gradual degradation of the Antarctic ecosystem. In addition, they are the basis for a discussion on the tightening of legal regulations regarding the protection of the Antarctic environment.

3. Introduction

Over the past decades, there has been increasing human impact in the Antarctic environment [1–3]. Although the Antarctic can presently be considered one of the least polluted areas in the world, a number of chemical pollutants, including persistent organic pollutants (POPs), have been proven to exist in both animate and inanimate elements of nature [2,4,5]. Among the POPs found in Antarctica, chemical compounds whose origin is associated solely with human activities should be distinguished, e.g. polychlorinated biphenyls (PCBs) [6–8] and organochlorine pesticides (OCPs) [8–10]. Particularly noteworthy are pollutants that come not only from anthropogenic sources but also from natural sources, e.g. polycyclic aromatic hydrocarbons (PAHs) [1,6,11,12].

Some elements [13–15] and inorganic ions are also chemicals with mixed emission sources. If they are present in excess in an environment where their natural concentration levels are lower, they too can be treated as pollutants that are also anthropogenic. Some inorganic ions such as Na^+, Cl^-, SO_4^{2-} are clearly related to the impact of marine aerosols off the Antarctic coast. In addition, anthropogenic and biological sources of SO_4^{2-} may be contributing through atmospheric transport [16]. The SO_2 can come from ship emissions and from stations and become a secondary source of sulphates by the oxidation of SO_2 to SO_4^{2-} [17]. In the Antarctic area, some toxic elements (e.g. As, Cd, Cu, Pb, Hg) usually come from accidental fuel spills [18] and the use of petrol engines [19]. It should be emphasised that these heavy metals in the environment originate from both human activity and natural sources. Due to the presence of many scientific stations and an increasing intensity of tourism in Antarctica, an anthropogenic impact on the chemistry of waters and sediments is inevitable [20].

Due to the simple method of wastewater disposal in many polar research stations, it is also worth paying attention to micropollutants that can be emitted into Antarctic ecosystems as a result of wastewater discharge. The concentrations of emerging contaminants (ECs), e.g. pharmaceuticals and personal care products (PPCPs) and illicit drugs in Antarctica has been little studied [21–23]. After human consumption, pharmaceuticals or their metabolites are excreted in urine and faeces. Personal care products are primarily intended for external use on the human body and therefore undergo

few metabolic changes [24]. In addition, 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 to, inter alia, personal care products, laundry and cleaning detergents [25]. Emerging contaminants (ECs) are therefore emitted to the Antarctic environment through the discharge of both treated and untreated wastewater. The harsh Antarctic climate, characterised by low temperatures, polar night periods and the presence of ice in the coastal seawater zone, may contribute to the limited degradation of these contaminants, which will result in their prolonged persistence in the environment [21]. Formaldehyde from agents and disinfectants may also be released into the wastewater as a result of maintenance of station buildings and daily activities. Due to its high reactivity, colourlessness, stability and low cost, formaldehyde has been applied as a resinification agent, curing agent, synthetic agent, disinfectant, fungicide and preservative [26]. Moreover, this aldehyde is highly toxic to living organisms; for example, it may damage DNA and cause mutations in microorganisms, and it poses a carcinogenic risk. Therefore, any wastewater containing formaldehyde might be toxic to microorganisms [27].

After emission, pollutants in the Antarctic environment may bioaccumulate in both animals [8,9] and plants [28] living in this area. Exposure to some of them in the Antarctic environment is a particular threat to Antarctic fauna and flora, since these chemicals (which are lipophilic) are bioaccumulative [29]. The accumulation of some pollutants in mosses [28,30] suggests that Antarctica may become an important absorber in the global chemical contaminants cycle. This may increase the environmental burden on pollutants, particularly in relation to the sensitive Antarctic environment. Cycles of long-range atmospheric transport (LRAT), deposition and reemission [31] can be repeated many times, which makes them a source of pollution in areas with insignificant anthropogenic activity, such as Antarctica, leading to the accumulation of these compounds [32,33]. It was proven that the transport of pollutants in the atmosphere can have a significant impact on the pollution load in the hydrosphere [34].

The toxicity [35] of some contaminants (e.g. heavy metals, PAHs) poses a real threat to organisms living in the Antarctic and thus to the balance of ecosystems in this

area. Also noteworthy is the fact that few living organisms have chemical pollutant detoxification mechanisms [36]. Therefore, it is important to determine the current spatial distribution of these chemical individuals and identify their potential sources. Abiotic elements of the environment such as snow, glaciers and polar catchments are sources of water for all living organisms in Antarctica. The Antarctic food web has a very simple structure, so even a small amount of pollutants found in abiotic elements of nature can pose a significant threat to any plant or animal species due to possible changes in detoxification mechanisms [37]. Antarctic species may be more susceptible to the effects of pollution than species native to temperate regions [38]. This is because their detoxification mechanisms are poorly developed (or not at all). Moreover, due to the very simple structures of polar ecosystems, close relationships between different organisms are important for the transport of pollutants [4].

As part of the doctoral dissertation, I have studied and described the processes of:

- directing contaminants to various elements of the Antarctic environment,
- defining pollutant sources,
- assessing the contribution of each source to the total content of individual xenobiotics and
- the environmental fate of these pollutants.

Therefore, a necessary element was the estimate of pollutant flux based on chemical analysis results, which is associated with supply from glaciers, seasonal supply from snowmelt, and anthropogenic impact. These mechanisms can be temporally and spatially diverse, and, therefore, dependencies of this kind were the subject of research conducted as part of this dissertation. In addition, natural sources of compounds classified as pollutants were also taken into account during the research and their contributions to supplying the environment were taken into account. From the whole of Antarctica, the western coast of the Admiralty Bay on King George Island (which is part of the South Shetland Islands) was selected as the area of research on the deposition of pollutants in individual components of the abiotic environment. The study area includes Antarctic Specially Managed Area 1 (ASMA 1) and Antarctic Specially Protected Area 128 (ASPA 128), which were established primarily due to the presence there of a unique set of birds

and marine mammals. ASMA 1 is a protected area in the Admiralty Bay area characterized by high environmental, historical and scientific values. ASPA 128 is located south of the Henryk Arctowski Polish Antarctic Station, and east of the Warszawa Icefield. Considering the long-term character of the research (years 2016–18), this doctoral thesis is a unique source of information on pollution identification, distribution and concentration variabilities occurring in ASMA 1, ASPA 128 and their surroundings.

Antarctic environmental chemistry monitoring allows for the control of – and even changes to – international legal regulations, the introduction of bans and restrictions, e.g. by the Scientific Committee on Antarctic Research (SCAR), the SCAR Group of Specialists on Environmental Affairs and Conservation (GOSEAC), and others. For example, some contaminants (e.g. OCPs) are target chemicals for the global monitoring plan of the United Nations Environmental Program (UNEP) Stockholm Convention for the global regulation of POPs [39]. It should be especially noted that there is a scarcity of pollutants-monitoring data (including for POPs) from the Southern Hemisphere and especially in Antarctica as compared to what is available for Arctic regions. This is because logistics (e.g. transporting monitoring equipment, costs for establishing and maintaining infrastructure and expert support) are more difficult and expensive in the Antarctic than in the Arctic. As the main goal was to verify the degree of pollution in Antarctica, it was necessary to perform the following:

- To evaluate in detail the actual state of contamination in Antarctica (literature review)
- To select the potentially affected environmental compartments (fresh water, sediments, snow cover, marine water)
- To verify hypotheses through environmental, chemometric analysis, etc.

To illustrate the multi-stage nature and complexity of the research carried out during the doctoral dissertation, a number of activities that were necessary to implement the research plan are presented in Fig. 1. Analyses and interpretations of the results obtained during the work related to this doctoral dissertation filled the gap in information regarding the state of the environment on the western coast of Admiralty Bay, which will contribute to efforts to reduce the anthropogenic impact on sensitive Antarctic ecosystems.

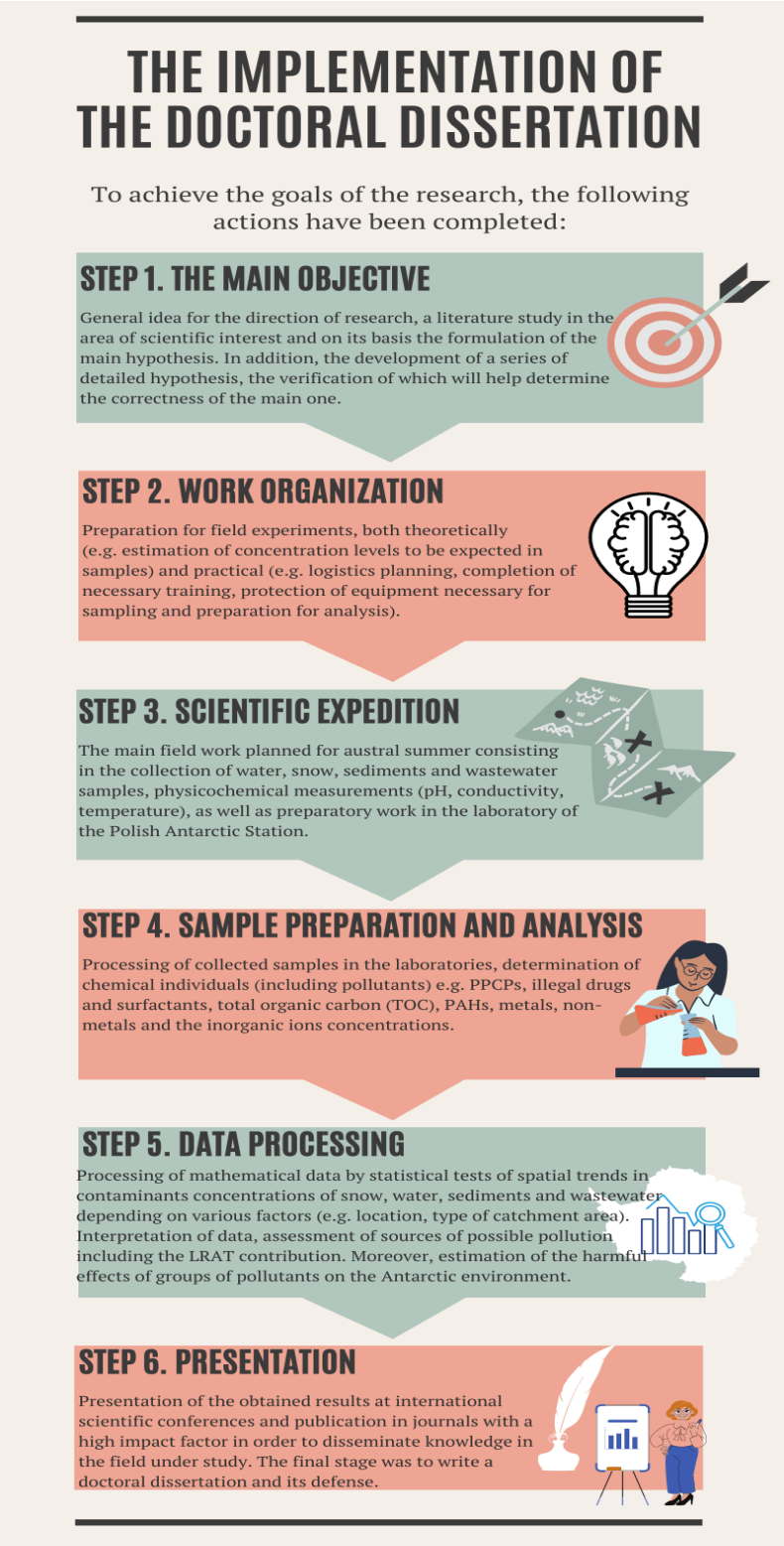

Figure 1. General description of activities undertaken to implement the research plan as part of the doctoral dissertation

4. The genesis of research work

4.1 Environmental research on contamination conducted in the whole of Antarctica

The abiotic environment (fresh- and seawater, rainfall, glaciers, soil) as well as all processes and phenomena related to changes in individual elements of the environment (meteorological, geological, geochemical processes) play a significant role in the transport of pollutants in Antarctica [4].

Atmospheric air also plays a significant role in transporting pollutants to the polar regions. Over the past decades, studies have been carried out to identify the mechanisms that contribute to the presence of pollutants in Antarctica and to distinguish pollution from local sources from that transported from remote areas. Most of the information on Antarctic air pollution comes from research conducted during expeditions near Antarctica and is based primarily on short-term (weekly, monthly) atmosphere monitoring. Long-term monitoring of atmospheric pollution in Antarctica is recommended, as this type of research is a significant scientific tool for assessing the anthropogenic environmental impact at a global scale.

Monitoring of these pollutants is important due to the accumulation of these substances in living organisms, their long persistence in the environment and their significant impact on the ecosystem [40]. Long-distance transport of pollutants is believed to be the cause of the presence of more volatile substances in Antarctica, and the presence of less volatile substances that occur occasionally in Antarctic air may indicate the influence of local sources [20]. Long-distance transport of pollutants occurs through successive evaporation, then wet and dry deposition, mediated by atmospheric transport [41]. This mechanism is known as LRAT.

On the basis of a detailed analysis of the collected literature, the dissertation hypotheses were formulated, and are presented in Chapter 5 “The aim of the doctoral dissertation”. A summary of the collected literature data was published in two publications (I and II included in this doctoral dissertation).

The first of the articles presented in the dissertation: **Potapowicz J., Szumińska D., Szopińska M., Polkowska Ż., The influence of global climate change on the environmental fate of anthropogenic pollution released from the permafrost. Part I. Case study of Antarctica, *Science of the Total Environment*, 651 (2019) 1534-1548**, concerns the specific role that the active layer plays in the migration of chemical compounds in the soil. Freeze–thaw cycles occur especially in the active layer of permafrost, as a result of which soil particles may undergo slow screening processes. Smaller particles can migrate from the surface layer to deeper layers, while stones tend to migrate from deeper layers to the surface. The pollutants are adsorbed mainly on the surface of particles of smaller diameters. In this article, we collected and analysed the results of studies that show that the percentage (amount) of small particles and their dynamics in the soil matrix are key determinants of the fate and degradation of pollutants (e.g. PAHs) in Antarctic soil. Thus, the thawing of the upper layer of permafrost caused by global warming will have a significant impact on the distribution of pollutants in this environment.

Another subject of the research described in **publication I** was the comparison of analytical studies conducted over the years in the Antarctic in terms of the types of samples and analytes that the studies determined. Another important aspect was the spatial analysis of pollutant distributions in Antarctica. Environmental monitoring enables reliable observation of changes, and the information contained in the publications relates to individual parts of the Antarctic ecosystem and various groups of pollutants.

In addition, we paid attention to the study of samples of biological origin, mainly due to the assessment of the real impact of pollutants on the Antarctic ecosystem and the identification of possible directions for the movement of pollutants in the food chain. The article highlights the presence of chemical pollutants in the tissues of organisms due to their toxicity and their being widespread in the biotic environment (both in fauna and flora). Their concentrations may also increase in the subsequent stages of the Antarctic environment food chain.

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Review

The influence of global climate change on the environmental fate of anthropogenic pollution released from the permafrost Part I. Case study of Antarctica

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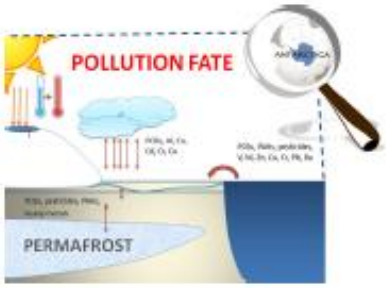
HIGHLIGHTS

- Permafrost distribution in Antarctica and reemission of pollutants
- Environmental fate of anthropogenic pollution remobilised from the cryosphere
- Pollution from permafrost present in the Antarctic affects the living organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

This article presents a review of information related to the influence of potential permafrost degradation on the environmental fate of chemicals species which are released and stored, classified as potential influence in future Antarctic environment. Considering all data regarding climate change prediction, this topic may prove important issue for the future state of the Antarctic environment. A detailed survey on soil and permafrost data permitted the assumption that this medium may constitute a sink for organic and inorganic pollution (especially for persistent organic pollution, POPs, and heavy metals). The analysis of the environmental fate and potential consequences of the presence of pollutants for the existence of the Antarctic fauna leads to a conclusion that they may cause numerous negative effects (e.g. Endocrine disruptions, DNA damage, cancerogenicity). In the case of temperature increase and enhanced remobilisation processes, this effect may be even stronger, and may disturb natural balance in the environment. Therefore, regular research on the environmental fate of pollution is required, especially in terms of processes of remobilisation from the permafrost reserves.

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Contents

1. Introduction

Permafrost, defined as soil, rock, or sediment that remains at or below 0 °C for two or more consecutive years, covers vast areas (Bockheim et al., 2013). Permafrost is most extensive in the Arctic, but also exists on the Central Asian Plateau and in ice-free areas of Antarctica, including the Antarctic Peninsula region (Bockheim et al., 2013). An impermeable barrier associated with permafrost prevents drainage and leads to the occurrence of high water table wetlands, lakes, and ponds (Vincent et al., 2011). Moreover, it affects the biogeochemistry and geomorphology of the landscape, and thereby biological productivity and biodiversity, especially in polar regions (Vincent et al., 2011; Dobiński, 2012; Chaves et al., 2017; Almeida et al., 2014, 2017; Correia et al., 2017).

Global climate changes and the related cryosphere degradation as the effects of temperature increase have been observed in both Northern and Southern Hemispheres over the last several decades (e.g. Serreze et al., 2000; Vaughan et al., 2003; ACIA, 2005; Turner et al., 2005; Mulvaney et al., 2012; IPCC, 2013; Kejna et al., 2013). Considering that permafrost underlines an area of 22 million km², processes related to the state and changes in permafrost concern a significant part of the global land area (approximately 17%) (Bockheim et al., 2013). Recent studies show that the periglacial zone is one of the most rapidly changing areas on earth (e.g. Cooper et al., 2011; López-Martínez et al., 2012; Karlsson et al., 2012, 2015; Oliva and Ruiz-Fernández, 2017; Ravanel et al., 2017; Oliva et al., 2018).

It should be emphasised that except for the relatively well known and thoroughly described influence of permafrost on water and soil chemistry in the internal region of the North America, Europe, and Asia (e.g., Carey, 2003; O'Donnell and Jones Jr., 2006; Petrone et al., 2006; Frey et al., 2007; McClelland et al., 2007; Frey and McClelland, 2009; Keller et al., 2010; Bagard et al., 2011; Douglas et al., 2013; Larouche et al., 2015; Manasypov et al., 2015; Szopińska et al., 2016; Lehmann-Konera et al., 2018), there is still little known about permafrost related geochemical processes and its role in shaping of the chemical status of areas recently uncovered by glaciers in the Antarctic and Arctic regions.

Research projects carried out in recent years resulted in numerous works regarding to the presence of permafrost in the Antarctica (e.g., Guglielmin and Cannone, 2012; López-Martínez et al., 2012; Bockheim et al., 2013; Guglielmin and Vieira, 2014; Guglielmin et al., 2014; Simas et al., 2015; Oliva and Ruiz-Fernández, 2017). Some papers pointed out that the ongoing trend of increasing air temperatures could affect soil organic matter (SOM) turnover and soil C-CO_2 emissions in the terrestrial ecosystems of Maritime Antarctica (Pires et al., 2017). Several studies prove that Antarctic seawater, snow, and presumably soils are becoming important secondary sources remobilising POPs (Cabrerizo et al., 2012, 2013; Klánová et al., 2008). They can also cause an increase in the concentration of legacy pollutants such as hexachlorobenzene and polychlorinated biphenyls (PCBs) in the Antarctic environment (Cabrerizo et al., 2013). A lot of international agreements have been passed to protect Antarctica. The Protocol on Environmental Protection to the Antarctic Treaty is the most notable of them. Since its implementation, importation of specific POPs has been prohibited, and also research stations and practices have been improved (Cabrerizo et al., 2012). Polycyclic Aromatic Hydrocarbons with a higher molecular weight, i.e. with 4–6 aromatic rings, are other contaminants highly toxic to organisms in the Antarctic environment. They have carcinogenic and mutagenic properties (Martins et al., 2010). Another group of pollutants which may be stored in permafrost and are hazardous to the environment consists of heavy metals. In the case permafrost-affected soils of Antarctica, it should be also emphasised that the freezing process may significantly influence the distribution of elements within the soil profile (Nagare et al., 2012).

Considering that inorganic and organic contaminants are temporarily stored in sediments and may be released into environment with the thawing and freezing of permafrost (e.g., Carey, 2003; O'Donnell and Jones Jr., 2006; Petrone et al., 2006; Frey et al., 2007; McClelland et al., 2007; Frey and McClelland, 2009; Keller et al., 2010; Bagard et al., 2011; Douglas et al., 2013; Larouche et al., 2015; Manasypov et al., 2015; Szopińska et al., 2016; Szumińska et al., 2018), this work presents an attempted comparison and summary of knowledge on potential influence of permafrost on the chemical status of the Antarctic ecosystem. Special attention was paid to sources of inorganic and organic compounds (natural or anthropogenic, local or long-distance) and their potential influence on Antarctic biota. The proposed summary could be important for understanding the potential environmental hazards associated with the accumulation of anthropogenic pollution in the Antarctic environment. Taking into consideration the holistic approach to the polar geomorphic system proposed by Dobiński (2012), we can assume that both processes – accumulation and release of contaminants - occur simultaneously, and contaminants are transferred continuously within the cryogenic environment.

2. Permafrost distribution in Antarctica

The map provided by Bockheim and Hall (2002) shows the ice-free area in Antarctica where permafrost can potentially occur, as well as the probable occurrence of subglacial permafrost (Fig. 1). Only 0.35%, or 45,000 km² of Antarctica is ice-free (Bockheim, 1995). Continuous permafrost occurs in continental Antarctica. Its thickness reaches 1000 m in the McMurdo Dry Valleys and 500 m on the Ross Island. In the Antarctic Peninsula permafrost is discontinuous, with a thickness ranging from 3 to 25 m on the Deception Island, 20–100 m on the King George Island, and 35–200 m on the Seymour Island (Bockheim et al., 2013). Detailed research on seasonal permafrost thawing shows

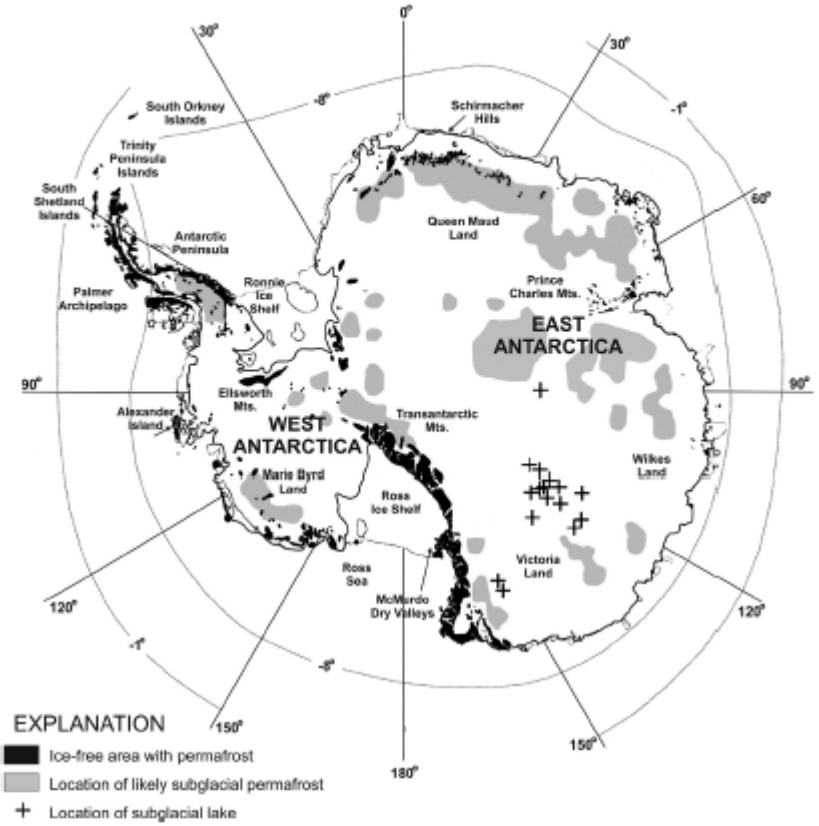


Fig. 1. Permafrost distribution in Antarctica (Bockheim and Hall, 2002). Ice-free areas are presented in black, probable distribution of subglacial permafrost beneath the Antarctic ice sheet is presented as shaded areas, subglacial lakes are depicted with a cross; The −8 °C and − 1 °C mean annual air temperature isotherms are taken from Weyandt.

different depths of the active layer, varying from 0 to 60 cm in the Interior Antarctica (Bockheim, 1995; Bockheim and Hall, 2002) to prevailing ranges between 10 and 200 cm in the Antarctic Peninsula (Vieira et al., 2010), in particular cases exceeding 600 cm (Bockheim et al., 2013). Moreover, Bockheim and Hall (2002) pointed out that the concept of an active layer is less relevant in interior Antarctica, because much of the permafrost in interior Antarctica is 'dry' in contrast to the Antarctic Peninsula and its offshore islands, and to maritime East Antarctica, where mainly wet permafrost occurs.

The detailed research conducted on the Antarctic Peninsula suggests that permafrost distribution in this area is largely controlled by local factors, such as marine disturbance (Vieira et al., 2010), duration and thickness of snow (Oliva et al., 2017a; Ferreira et al., 2017), land relief (Oliva et al., 2017a), lithology (Hrbáček et al., 2017), and vegetation cover (Almeida et al., 2014). Lithological conditions influence among others the average depth of active layer thickness. This layer in the South Shetland Islands usually exceeds 100 cm in loamy soils (de Pablo et al., 2013; Schaefer et al., 2012; Oliva et al., 2017b). The deepest active layer (>300 cm) was observed in bedrock in the vicinity of Bellingshausen site, located in the western region of the King George Island (Hrbáček et al., 2018). The active layer is the thinnest on the Deception Island, located in the South Shetland Islands archipelago. It reached only 30–50 cm (Ramos et al., 2017). According to some authors, the ocean influence limited permafrost occurrence at the sea coast (Correia et al., 2017; Ferreira et al., 2017; Strzelecki et al., 2018). However, several papers indicate geomorphological formations and soils evidencing permafrost-related processes in the ice-free area at low altitudes, e.g. seasonal thawing-freezing affected soils (Simas et al., 2015), patterned grounds (Dąbski et al., 2017), and frost mouds, sorted circles and stripes (Oliva and Ruiz-Fernández, 2017). Bockheim (1995) summarised that periglacial features related to freezing and thawing processes occur in the Antarctic as: gelifluction features (lobes, terraces, and sheets); patterned ground features (sorted and non-sorted circles, sorted and non-sorted polygons and nets, sorted polygons and nets, sorted steps, sorted and non-sorted stripes); ground ice features (ice wedges, rand wedges, rock glaciers, pingos, thermokarst, ice-cored drift). Inactive periglacial features also occur in Atarctic, namely: ice-wedge casts, inactive patterned ground, inactive rock glacier, inactive solifluction features.

The last of the mentioned formations as well as glacier retreat constitute evidence of climate change observed over the recent decades on the Antarctic Peninsula (e.g., Vaughan et al., 2003; Cook et al., 2005; López-Martínez et al., 2012; Mulvaney et al., 2012; Bockheim et al., 2013; Chaves et al., 2017; Pętlicki et al., 2017; Hrbáček et al., 2018; Szopińska et al., 2018). Mean annual air temperature along the western Antarctic Peninsula increased by as much as 3.4 °C, and mid-winter temperature increased by 6.0 °C over the past 50 years, making the region one of the most affected by climate warming (Vaughan et al.,

2003; Turner et al., 2005). Permafrost degradation was reported on the Antarctic Peninsula, even to the point of its disappearance at sites near the Palmer station (64°77'S) (Bockheim et al., 2013). Permafrost was much colder (−3 °C) southwards, close to the Rothera research station (67°57'S) with an active layer ranging between 0.76 and 1.4 m (Guglielmin et al., 2014). Guglielmin and Vieira (2014) concluded that the active layer thickness is directly proportional to the mean summer air temperature, and inversely proportional to the maximum snow depth in autumn. Recent research has also shown much greater permafrost dynamics in the Antarctic environment, associated with the generally high dynamics of morphological processes in the area (Bockheim et al., 2013; Chaves et al., 2017; Almeida et al., 2014, 2017).

3. Environmental fate of anthropogenic pollution remobilised from the cryosphere

Recent decades have shown phases of the most rapid warming on the Antarctic Peninsula (Mulvaney et al., 2012; Bockheim et al., 2013). This raises a concern, especially in reference to potential changes in sea ice coverage and concurrent increase in anthropogenic emissions of contaminants from the southern hemisphere (Bargagli, 2008). This could enhance the transport and deposition of persistent contaminants in Antarctica (Xue et al., 2016). As already mentioned, the present chemical status of surface water in the Antarctic region is the effect of contemporary transport of pollutants, as well as the release of previously accumulated contaminants from glaciers and permafrost thawing (Herbert et al., 2006; Curtosi et al., 2007; Martins et al., 2010; Xue et al., 2016). It is assumed (Bengtson Nash, 2011) that Persistent Organic Pollutants (POPs) contained in permafrost may have their source in anthropogenic activities since the mid-1900s. Because of their toxicity, extreme persistence and bioaccumulation capacity, this compounds spread, what have resulted in contamination of Antarctic environment. Some of the pollutants stored in permafrost can also come from natural sources, as described in detail in the Subsections 3.1, 3.2 and 3.3 of this work. Climate change can also cause the intensification of the rate of glacier ablation and melt, resulting in higher concentrations of organic compounds from atmospheric deposition accumulated in meltwater, and then in glacier-associated persistent pollutants accumulated on the meltwater surface after the ice retreats or melts. Moreover, increased rain and thawing processes caused by global warming could cause a significant soil-associated mobilisation of pollution, which could in turn have unpredictable knock-on effects on biota (Curtosi et al., 2007). Processes of contamination transport within abiotic media are presented in Fig. 2.

Based on literature data (Bargagli, 2008; Corsolini, 2009; Szopińska et al., 2017; Bengtson Nash, 2011), two main groups of contaminants can be distinguished which may be stored and/or remobilised from permafrost, namely persistent organic pollution (POPs) and heavy metals.

POPs are toxic compounds produced by the industry and released to the environment through antropogenic activities. They are resistant to degradation, so they can accumulate in the environment over long periods of time in solid, liquid, or gas-phase reservoirs from which they pose risks to ecosystems and human health. Global contamination with POPs of all environmental matrices is caused by their extreme persistence and effective environmental dispersal mechanisms (Bengtson Nash, 2011). These contaminants include chemicals such as polychlorinated biphenyls (PCBs), pesticides, polycyclic aromatic hydrocarbons (PAHs), and unintentionally produced chemicals (such as dioxins and furans) (Bengtson Nash, 2011). The accumulation of semi-volatile chemicals in cold environments is caused by thermodynamic forcing by temperature gradients (Bengtson Nash, 2011; Ma et al., 2016). The authors also concluded that the long half-lives of these chemicals facilitate repeated cycles of volatilisation and deposition, which results in movement of semi-volatile chemicals away from temperate and tropical source regions towards colder climates. Bengtson Nash (2011) and Ma et al. (2016) point out that these compounds may be subject to "cold-trapping" in polar areas or at an altitude where colder temperatures further prolong their persistence.

Metals of anthropogenic origin, predominant in various components of the Antarctic environment are as follows: Cr, Ni, Cu, Zn, Pb, Cd (Chaparro et al., 2007). Hg is also noteworthy, not because of high concentrations in the environment, but because of its high toxicity (de Ferro et al., 2014). According to research by Lu et al. (2012), the average concentration of mercury in soil sampled from Fildes Peninsula is 0.0221 ng/g. Metals may affect biological processes positively or negatively, depending on their concentration. Trace elements in soils originate from natural and anthropogenic sources. The load of metals in the soil depends on the type of metal and soil, as well as on the subsequent accumulation of the metal in other elements of the environment. It has been proven that excessive levels of metal pollution in the environment may not only have negative effects on the soil's fertility, but also cause ecological and human health risk (Robinson et al., 2005). In Antarctica, sediments and soils are a major reservoir for metals. Therefore, they are an excellent source of information about the load of metal pollution over the years. Some sediments can also act as a source of contaminants (Santos et al., 2007). Antarctica plays a significant role in the determination of global contamination levels and trends. Natural baseline levels of metals in the Antarctic environment are a gauge of changes in their global concentration (Lu et al., 2012).

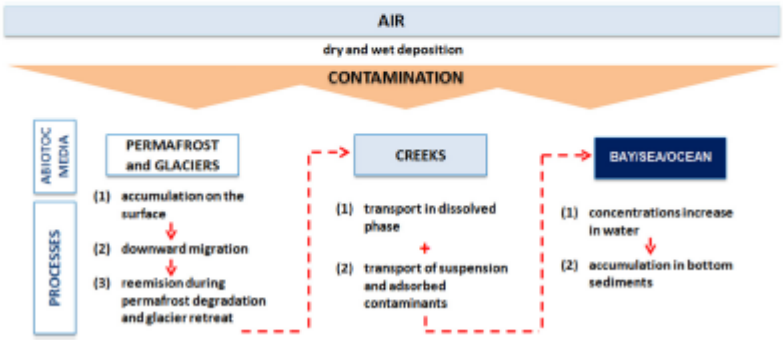


Fig. 2. Environmental fate of contamination delivered to Antarctica via long-range atmospheric transport (LRAT) in abiotic components.

3.1. Pesticides and trace PCBs

Polychlorinated biphenyls (PCBs) belong to the group of organochlorine compounds. The emissions of PCBs and pesticides are successful curtailing, although the chemicals still pervade global ecosystems. These compounds are present also in Antarctic. They generally come from LRAT via precipitation and cold condensation. Moreover, snow also has influence on the deposition and the fate of PCBs in cold environments (Klánová et al., 2008).

Contemporary research (e.g. Cabrerizo et al., 2013; Bengtson Nash, 2011; Klánová et al., 2008; Ma et al., 2011) suggests that the existence of many sources of PCBs and pesticides contamination in the Antarctic areas. First of all, polar regions receive the chemicals through atmospheric transport and deposition, and are accumulated in soils, ice, and waters. Nonetheless, contemporary research (Geisz et al., 2008; Ma et al., 2011; Cabrerizo et al., 2013) on polar regions has shown evidence that historical burdens of PCBs and pesticides are currently being remobilised from retreating permafrost cover in Antarctica. This remobilisation may be enhanced under climate change and result in an increase in their availability for exchange with the atmosphere, whereby the ecosystem's exposure to previously immobilised PCBs and pesticides is increasing (Noyes et al., 2009; Cabrerizo et al., 2013). Moreover, due to the intensifying effect of climate warming, vapour pressure increases, resulting in an alteration of the thermodynamic equilibria for partitioning of PCBs among various environmental media (Ma et al., 2016) and e.g. their distribution into aquatic environment.

According to Klánová et al. (2008), whose research included the James Ross Island area, soil concentrations of PCB ranged between 0.510 and 1.82 ng/g. Cabrerizo et al. (2012) studied soils from the surface layer and 5 cm under its surface from the Livingston and Deception Islands. According to the authors, PCB concentrations were between 0.005 and 0.320 ng/g. Studies covering soils from the eastern part of Antarctica (Borghini et al., 2005; Negoita et al., 2003) suggest that levels of PCB contamination were similar to those in West Antarctica, as presented in Table 2. Cabrerizo et al. (2012) showed that the concentrations of pesticides in soils from the western part of Antarctica are significantly lower compared to PCB concentrations. According to the authors, hexachlorobenzene (HCB) concentrations fluctuated in the range of <LOQ-0.07 ng/g, while concentrations of p,p'-Dichlorodiphenyldichloroethylene (p,p'-DDE) from loq to 0.20 ng/g. Borghini et al. (2005) and Negoita et al. (2003) stated the presence of HCB and p,p'-DDE in soils from East Antarctic in concentrations: 0.02–25 ng/g, and 0.03–4 ng/g, respectively.

Chemicals present in soil after remobilisation may pass into water, the food web, and then top aquatic predators. Aquatic food webs are particularly prone to the biomagnification of PCBs (Ma et al., 2016). PCBs and organochlorinated pesticides (OCPs) bioaccumulate through food webs and reach significant levels in top predators because of their lipophilicity (Klánová et al., 2008). Furthermore, PCBs were among the earliest groups of man-made chemicals to be encountered in food webs. These compounds are the most widespread in the environment and biota, compared with others POPs (Baert et al., 2013). It

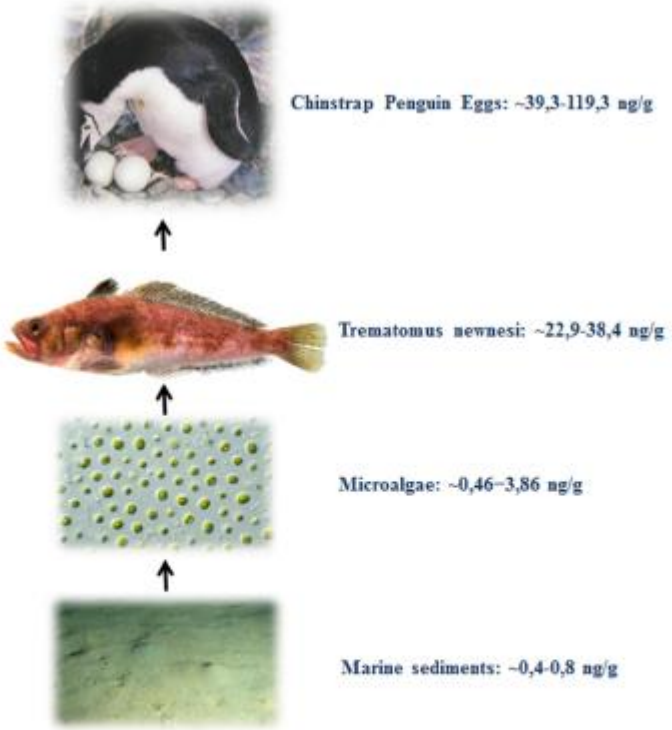


Fig. 3. Schematic view of ΣPCB bioaccumulation and biomagnification in Antarctica's marine food. Sources of PCBs concentrations are microalgae (Cabrerizo et al., 2012); marine sediments (Klánová et al., 2008); *Trematomus newnesi* (Lana et al., 2014); and Chinstrap Penguin Eggs (Mello et al., 2016). Pictures accessed from the websites: http://fishphylogenetics.blogspot.com/2012/09/an-adaptive-radiation-on-ice.html, http://hmsc.oregonstate.edu/research-labs/reimers-lab/current-research, http://www.animalspot.net/chinstrap-penguin.html, https://en.wikipedia.org/wiki/Microalgae.

is due to their durability in the environment and persistence to common (bio)-degradation pathways (Baert et al., 2013). In the Antarctic marine food web, biomagnification proceeds e.g. from microalgae to fish (*Trematomus newnesi*), with the higher trophic levels contributing to the traditional diet of Chinstrap Penguin (Fig. 3), therefore posing risk (Mello et al., 2016). Indirect connections exist between climate change and PCBs contamination to wildlife. An example is migration of marine species caused by climate warming and loss of ice cover (Cabrerizo et al., 2012; Lana et al., 2014; Mello et al., 2016). The effect may be altered exposure to PCBs on account of eating organisms containing high concentrations of PCBs, even if the migratory transport of the chemicals is small relative to quantities transported by other ways (Cabrerizo et al., 2012; Klánová et al., 2008). The altered climate of Antarctic also entails certain changes in the type of food consumed. Studies on levels of concentration in the tissues of birds inhabiting Antarctic proved that transequatorial migrant species such as skuas (*Chataracta* spp.) have higher PCBs burdens than penguins (*Pygoscelis* sp.). Based on the above, migratory seabirds, e.g. south polar skua, can affect a vehicle transport of chemicals. The result is contaminants of PCBs and pesticides from the northern regions to Antarctica (Mello et al., 2016).

3.2. Polycyclic aromatic hydrocarbons and alkanes

Any human activity in Antarctica, even limited to conducting scientific research, carries with it environmental risks associated with the use of fossil fuels. Scientific operations and the related logistic support require using them as an energy source for heating and lighting at the research stations, as well as a fuel for research boats, terrestrial vehicles, and re-supply vessels (Curtosi et al., 2007; Martins et al., 2010). In a year, fuel consumption by research stations amounts to approximately 90 million l 75% of which is diesel fuel (Martins et al., 2004). Increasing tourist activities in Antarctica and fisheries may also cause a risk for direct releases of hydrocarbons to the environment (Curtosi et al., 2007). In order to determine the record of human activities and remote contamination transported to the Antarctica, it is necessary to apply appropriate indicators such as concentrations of specific groups of polycyclic aromatic hydrocarbons (PAHs), alkanes, and even spheroidal carbonaceous particles (Martins et al., 2010). These compounds are transported to surface sediments by binding with suspended particulate matter in the water column (Martins et al., 2010). They are rarely found as products of biosynthesis. These compounds reach the marine environment mainly by human activity, and due to their properties they have a toxic effect on the environment (Martins et al., 2004).

Although Antarctica is considered as one of the most pristine areas of the world (Pongpiachan et al., 2017), several previous works (Martins et al., 2004; Cripps and Shears, 1997; Kennicutt et al., 1991) reported sporadic hydrocarbons pollution events (e.g. oil splits) in various components of this environment. Moreover, PAHs are produced in the process of fossil fuel combustion, especially during the process of its incomplete combustion. Fossil fuels are the most widespread source of energy in the southern hemisphere. PAHs generated in combustion processes enter the Antarctic environment, disturbing the functioning of ecosystems, as detailed in Chapter 4. Due to this, these compounds are one of the most important anthropogenic contaminants of the Antarctic environment (Martins et al., 2004; Martins et al., 2010). The compounds can also be formed during the combustion of wood and other organic materials (Curtosi et al., 2007). Anthropogenic sources of PAHs in the marine environment and soils of Antarctic are sewage discharge, vehicular emissions, and spillages of petroleum and its by-products containing complex mixtures of petrogenic PAHs (Martins et al., 2004; Martins et al., 2010). Although these external sources of hydrocarbons do not originate from the territory of Antarctica but at a considerable distance from this area, hydrocarbons are transferred to the Antarctic environment on account of LRAT (Martins et al., 2004). Little information about the natural sources of PAHs in the Antarctic environment has been found in the literature. Based on the work of Cabrerizo et al. (2012), one can assume that the significant source of these compounds may be the eruptions of the volcanos e.g. on Deception Island. In the case of n-alkanes, in addition to anthropogenic sources such as diesel oil degradation, there are also ones of biogenic origin, identified in many species of marine organisms. N-alkanes from biogenic sources are variable depending on the organisms present in a given study area (Martins et al., 2004). All hydrocarbon sources mentioned above (natural or anthropogenic) originate from local activities in Antarctica and therefore they can be classified as so-called in situ sources.

Some studies (Martins et al., 2004; Cripps and Shears, 1997; Kennicutt et al., 1991) on hydrocarbon contaminants discuss past incidents of oil spills in Antarctica which have caused severe localised effects on the fauna and flora, e.g. reduction of the survival of species and ecosystems (Cripps and Shears, 1997). It was also evidenced that such effects were of short-term character, and the recovery was rapid (Martins et al., 2004). Cripps and Shears (1997) showed that a diesel spill at Faraday Research Station that occurred on 2 March 1992 caused immediate toxic effect in the intertidal zone. However, because fuel dispersed quickly, as a result of evaporation, solution, and dispersal, the best strategy for small coastal fuel spills is initial cleaning followed by leaving the rest of the fuel to natural degradation processes.

Anderson et al. (1978) described the process of a slow sieving in permafrost, which happens because of repetitive cycles of freezing and thawing. Authors stated that during this process, small particles of soil migrate from surface to depth. In research of Krauss and Wilcke (2002), it was proved that PAHs are most of all adsorbed to the smallest particles. Additionally, Biggar et al. (1998) and McCarthy et al. (2004) hydrocarbon migration mechanisms are based on the gravity drainage through interconnected air voids in permafrost and in a minor extent the diffusion of this compounds in liquid water in soil, because permafrost is a barrier to water flow.

Cabrerizo et al. (2012) found the presence of PAHs on the Deception Island, Livingstone Island near Juan Carlos I Station, and Byers Peninsula (an Antarctic Specially Protected Area) in soils, mosses, lichens, algae, and some local plants. Researched by Curtosi et al. (2007) focused on soils from the vicinity of the Jubany Station and sediments from Potter Cove. The soil was taken from various depths. In the environmental samples, 25 compounds from the PAHs group were determined. Fourteen of the compounds were found in soils and six in marine sediments. Pongpiachan et al. (2017) also studied concentrations of PAHs in soil samples collected near the Great Wall Station (Chinese research station) located on the Fildes Peninsula on the King George Island. Martins et al. (2004), in addition to determining the concentration of PAHs, also confirmed the presence of aliphatic hydrocarbons in marine surface sediments around the Brazilian station in the Admiralty Bay. Bícego et al. (2009) studied concentrations of PAHs and hydrocarbons in water and sediments from the Admiralty Bay near research stations on the King George Island operated by Brazil, Poland, Peru, the United States of America, and Ecuador. The authors monitored the concentration of the compounds for 15 years. Table 1 presents results of PAHs content in soil from East and West Antarctic regions. The majority of the studies were performed in the South Shetland Archipelago region. There and other study results from West Antarctica are presented in Table 1. Based on this analysis it was found that levels of PAHs were variable in time and space. Since 2004, for the following 3 years, the minimum values of these compounds in western Antarctica have generally remained at the same level. A disturbing increase in the maximum concentration of PAHs occurred, however, in the years 2004–2009 in areas near the Antarctic research stations on the Antarctic Peninsula. The comparison of concentrations of PAH from 1999 and 2005 from eastern Antarctica shows a decrease in the level of soil pollution with these chemical compounds, both in terms of minimum and maximum values. From 2004 to 2009 in western Antarctica, a rapid increase in maximum concentration occurred from 45.0 to 3718 ng/g. Curtosi et al. (2007) concluded that rapid drainage of porous soils developed as a result of rainfall and melting snow and ice during summer could cause a

Table 1
PAHs concentrations in soils [ng/g dry weight].

Sampling area/Antarctic region	Year of research	Minimum value of ΣPAHs	Maximum value of ΣPAHs	References
Scott Base (Ross Island)/East Antarctic	1999	41	8105	Aislabie et al., 1999
Jubany Station (King George Island, South Shetland Islands)/West Antarctic	2004	11	45	Curtosi et al., 2007
Jubany Station (King George Island, South Shetland Islands)/West Antarctic	2005	11	588	Curtosi et al., 2007
Scott Base (Ross Island)/East Antarctic	2005	34.9	171	Klánová et al., 2008
Jubany Station (King George Island, South Shetland Islands)/West Antarctic	2007	10	1182	Curtosi et al., 2007
Juan Carlos I (Livingston Island, South Shetland Islands)/West Antarctic	2009	0.59	3718	Cabrerizo et al., 2012
Great Wall Station (King George Island, South Shetland Islands)/West Antarctic	2014	1.59	4.83	Pongpiachan et al., 2017

considerable inter-annual change in PAH concentrations in soils. They also linked high concentrations of these compounds to local sources of pollution such as accidental diesel spillage and low-temperature combustion of organic materials. Cabrerizo et al. (2012) showed that the mean concentrations of PAH in soil samples are in the range of 0.59–25.5 ng/g dw. They also stated that the exceptionally high PAHs concentration (3718 ng/g dw) detected in one sample is probably related to the fact that the soil samples were collected in the area where fossil fuel is usually stored, which might suggest accidental spillages. Moreover, Curtosi et al. (2007) pointed out that the active layer/permafrost transition zone showed the highest level of PAHs, and permafrost was revealed to be a low-permeability barrier to downward migration of these compounds. The thawing of the upper layer of permafrost, however, would have deep consequences in the transport and fate of the PAHs spilled on Antarctic soils, and would result in an increased flow of PAHs to coastal marine environments with unpredictable ecological consequences. In water, organic compounds such as PAHs and n-alkanes can be easily transported and accumulated in marine (Xue et al., 2016) and lake (Yao et al., 2016) sediments.

The presence of PAHs in such a pristine environment is even visible in penguins (Montone et al., 2016). Montone et al. (2016) have investigated the presence of PAHs in the main three species of penguins: the Gentoo (*Pygoscelis papua*); the Chinstrap (*Pygoscelis antarcticus*), and the Adelie (*Pygoscelis adeliae*) which constitute 95% of the biomass of breeding communities in this area (Sander et al., 2005). The levels of concentration in the fat are up to 238.7 ng g^{-1} wet weight. This evidences that PAHs, while moderately persistent in the environment, can be bio-accumulated. This phenomenon is also observed in fish fat tissues, e.g. in rock cod fish (*Trematomus bernacchii*) – 1520–1840 ng g^{-1} lipid wt (Hale et al., 2008). PAHs in penguins were dominated by two- and three-aromatic-ring compounds (Montone et al., 2016).

The literature provides no information on PAH concentrations after 2014. However, due to the increase in human activity in the regions of Antarctica, monitoring the level of concentration of these compounds can help improve and enhance legal acts protecting the environment of Antarctica.

3.3. Heavy metals and other elements

Heavy metals are a natural part of the Earth's crust. Based on the results of Lu et al. (2012); Carrasco and Prendez (1991); Zhao et al. (1989), Santos et al. (2005), Crockett (1998), it can be concluded that the dominant trace metals in the Antarctic environment are Al, Ca, Cd, Cr, Cu. These elements can get into the Antarctic environment via long-distance atmospheric transport and global circulation (Lu et al., 2012), and as a result of human activity in the vicinity of polar stations. Some of them (e.g. Al, Cu) can be considered to be of natural origin (Szopińska et al., 2018). Research on soil samples (Martins et al., 2002; Alam and Sadiq, 1993; Tin et al., 2009) has shown the relationship between the presence of several metals e.g. V, Ni, Zn, Cu, Cr, Pb, Ba with petroleum contamination. Potential sources of contamination with Pb and Cu include paints used for painting the internal and external surfaces of building walls (Webster et al., 2003). Point sources of Pb, Zn, and Cu in soils can be used batteries and rubbish resulting from activities in McMurdo Sound region (Santos et al., 2005). The main source of Pb in the Antarctic environment is fuel combustion. Hong et al., 1998 also stated that the source of Pb transported from areas distant from Antarctic is industrial activity and fuel consumption in large urban centers in South America. Several studies (Santos et al., 2005; Abakumov et al., 2017; Kennicutt et al., 1995; Lenihan, 1992) showed that concentrations of metals in sediments around the sewage outfall were higher than in sediments from areas far from the station, so another important source of metals is sewage. Not all research stations can use wastewater treatment plants. An increased concentration of trace elements, and particularly mercury, was observed in soils from the vicinity of Antarctic research stations that discharge untreated wastewater directly into the environment (Abakumov et al., 2017). Land relief has an effect on retention of these elements in the soil. On the other hand, anthropogenic input of organic matter to sediments favours sulfide formation, causing reduction of metal bioavailability, and consequently reducing adverse effects on local biota (Santos et al., 2005).

Numerous studies on the King George Island (e.g. Lu et al., 2012; Santos et al., 2005; Abakumov et al., 2017) proved that, as a result of human activity, large loads of elements are introduced into the Antarctic environment. Anthropogenic activity significantly affects the concentration levels of various elements in the environment, and makes it difficult to assess, whether the metals originate from natural or anthropogenic sources. Sediments and soils are major reservoirs for metals. They act as indicators of the quality of the environment (Santos et al., 2005). On the other hand, research by Szopińska et al. (2018) and Nędzarek et al. (2014) shows that the Arctowski Station (Polish Antarctic Station, King George Island) does not cause a significant increase in metal specific concentration (e.g. Pb). The studies evidenced that the recorded increased concentrations of trace elements may be associated with natural processes, and not necessarily with anthropogenic pollution such as researchers' activities. According to Lu et al. (2012), Nędzarek et al. (2014), by an equilibrium is possible to maintain metal values in Antarctic soils on baseline levels. The authors also concluded that this is caused by physical, e.g. mechanical erosion (Szopińska et al., 2018; Anderson et al., 2000), chemical e.g. geochemical weathering, of volcanic rocks (Nędzarek et al., 2014), as well as biological processes (Malandrino et al., 2009) occurring in the soil environment and interactions between them.

Another natural source of metals in Antarctic environment is birds, which have been determined to play a significant role in the alteration of chemical composition of soils and sediments. Such conclusions were drawn from research on the content of trace metals in guano. Some vascular plants, e.g. Antarctic hair grass (*Deschampsia Antarctica*), can concentrate some trace elements. These plants can be collected by birds, transported, and used to build nests. Based on the aforementioned circumstances, trace elements were found to be accumulated in ornithogenic soils (Abakumov et al., 2017).

According to Bockheim and Hall (2002), the process of soil formation in Antarctic is evidently slower in comparison to other continental environments. According to the literature, soil development as well as chemical and mineralogical changes in Antarctic are inhibited by factors

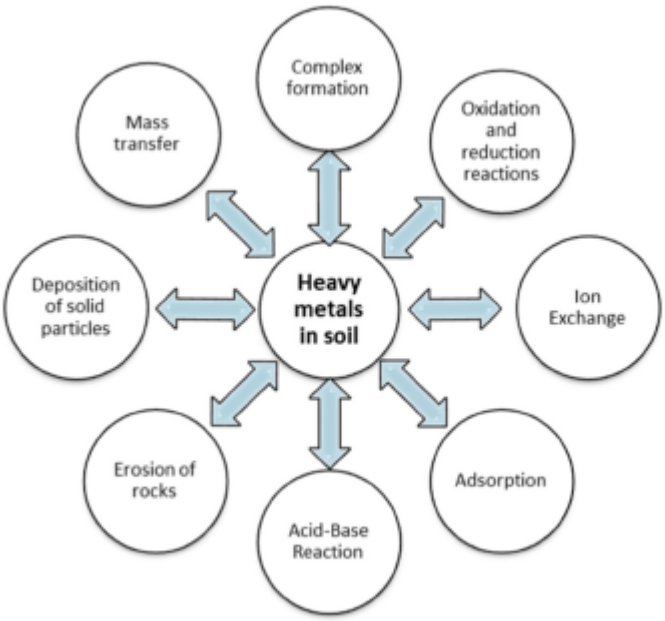


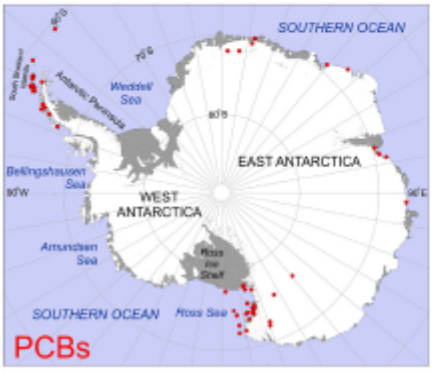
Fig. 4. A diagram presenting processes by which heavy metals pass to the soil (McLean and Bledsoe, 1992; Robinson et al., 2005; Nagare et al., 2012).

such as low temperature and limited quantity of liquid water (Navas et al., 2008; Simas et al., 2006; Vennum and Nejedly, 1990), characteristic of this area. As shown in Fig. 4, there are some further processes, including ligand exchange, adsorption, precipitation, and acid-base reactions, which have an effect on the distribution of dissolved and particulate metals in soils. Research by Basta and McGowen (2004) and White et al. (2012) shows that the mobilisation of some trace metals in soil (e.g. As or Sb) is caused by changes in the pH or redox conditions. For example, accumulation of birds and penguins guano promotes soil acidification (Poggere et al., 2017). Although pH of fresh guano is alkaline, it is quickly acidified up to a pH value of 4.0 as a result of sulfuric and nitric acid formation caused by its biological stabilisation on the ground (Tatur, 1989). As a result of guano accumulation, the chemical weathering process in the clay fraction becomes more intense. This in turn increases the intensity of short-range order phases (Poggere et al., 2016). Their characteristic feature is highly specific surface, where groups that are reactive e.g. silanol (eSiOH), aluminol (eAlOH), ferrol (eFeOH) are present (Poggere et al., 2017; Wada, 1989). These reactive groups present in the Antarctic environment have been evidenced to cause an increase in the intensity of adsorption of heavy metals (Mendonça et al., 2013). In addition to soil acidification in the Antarctic environment, guano also causes leaching of exchangeable bases, and transformation of primary minerals. According to Mendonça et al. (2013), metals (e.g. Fe, Al) in the form of ions or amorphous metals are released into the soil environment, and then bind to phosphorus compounds derived from ornithogenic activity forming compounds such as leucophosphite [$KFe^{3+}{}_2(PO_4)_2(OH)\cdot 2H_2O$] and metavariscite [$AlPO_4\cdot 2H_2O$].

Moreover, a relationship has been observed between the content of total organic carbon (TOC) in soil samples and the concentration of some heavy metals, e.g. Hg (de Ferro et al., 2014). The chemical processes of metals in Antarctic soils are governed by processes such as adsorption on various solid phases and reactions with organic matter. As a result of the latter, complexes and metal chelates are formed, quite persistent in the environment, and precipitation of compounds, generally stable or moderately soluble, occurs (Bradl, 2004). Poggere et al. (2017) have recently shown that in permafrost-affected areas of Antarctica, erosion of rocks plays a significant role in the transport of trace metals. For example, as a result of pyrite oxidation (FeS), a sulphate is formed and minerals such as jarosite [$KFe^{3+}{}_3(SO_4)_2(OH)_6$] and natrojarosite [$NaFe^{3+}{}_3(SO_4)_2(OH)_6$] precipitate (Simas et al., 2006).

According to research from permafrost areas (e.g. Panin and Kazantsev, 1986; Ostroumov et al., 1998; Ostroumov et al., 2001; Streletskii et al., 2003), the transport of metal ions in long-term permafrost in the Antarctic is closely related to the movement of water. It is possible through water films adsorbed by soil particles. Water films can then transport these chemical entities. In many scientific studies (e.g. Cary and Mayland, 1972; Chamberlain, 1983; Henry, 1988; Marion, 1995) regarding the redistribution of soluble components in permafrost-affected soils, a dependence was observed between freeze-thaw processes and selected chemical elements in soils. Water transport in freezing soils particularly takes place through the capillary phenomena. Cryogenic suction occurs through a pressure deficit or negative pressure. In Antarctic soils affected by permafrost, the temperature gradient does not change despite seasonal changes of its direction in autumn and spring (Antcibor, 2014). A decrease in heat input to the surface soil horizons in autumn causes downward freezing from the top soils, and upward freezing of the active layer from the permafrost table. The migration process of water molecules in the soil profile depends on their movement from the unfrozen side to the frozen side along with water films adsorbed to soil particles. If the soil begins to freeze, water that is least attached to soil particles freezes first. Then in the soil pore spaces, ice crystals are formed. Many studied (e.g. Illuminati et al., 2016; de Oliveira et al., 2017; Vodopivez et al., 2015; Husmann et al., 2012) discussed the occurrence of heavy metals in the tissues of living organisms. According to Goutte et al. (2015), the concentrations of trace elements increase along with higher trophic level

of organisms as a result of bioaccumulation and bioamplification processes within trophic webs occurring in Antarctica (Atwell et al., 1998; Morel et al., 1998). Moreover, that level of exposure to trace metals was found to be dependent on the foraging habitat (Goutte et al., 2015). For example, fish species inhabiting the benthic boundary layer will have a higher level of Hg in the tissues than those foraging in the water column and underneath sea ice (Fitzgerald et al., 2007). Seabirds were evidenced to be excellent bioindicators of Hg pollution (Burger and Gochfeld, 2004), because feathers are the main route of Hg excretion in birds (Monteiro and Furness, 1995). Research by Carravieri et al. (2013) showed that in long-lived animals, Hg can bioaccumulate in their tissues over their whole life span. The mechanism of metal accumulation was also observed in the tissues of lichens (Guerra et al., 2011). The authors concluded that some chemicals naturally occurring in lichens, e.g. usnic, pulvinic, and rhizocorpic acids, can promote the formation of stable complexes with metals. Grotti et al. (2008) showed that as a result of low temperature of Antarctic water, specific ways of feeding, and longevity, the bioaccumulation of metals in Antarctic organisms may be more intense than in other environments.



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LI 8
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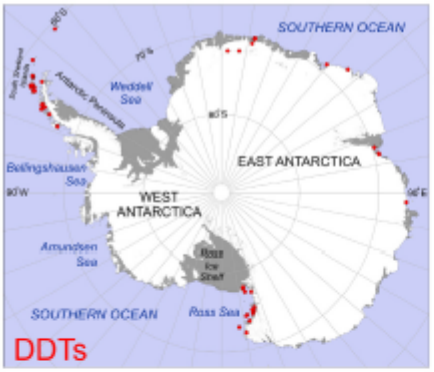
Others 26



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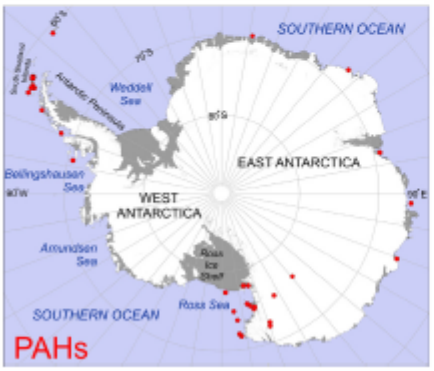

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KGI 17
LI 3
VLRS 20
Others 14

4. Possible environmental consequences of the presence of contaminants released from permafrost or the cryosphere

Recent years have seen higher temperatures (Chapman and Walsh, 2006; Turner et al., 2005) and changing stocks of soil organic matter (SOM) on the Antarctic Peninsula (Vaughan et al., 2003; Hill et al., 2011; Cabrerizo et al., 2012). This is probably related to a number of factors such as changes in the soil metabolism, changes in vegetation cover, or increase in impact from human settlements. A significant change has been observed in the extent of terrestrial biota habitats in the Antarctic Peninsula (Cabrerizo et al., 2013; Hill et al., 2011). This is exemplified by growth rates of lichen *Usnea Antarctica*. On the Livingstone Island, its annual growth rate in length of 2 mm per year with an increase in the lichen diameter from 50 in 1991 to 72 mm in 2002 was observed. This is probably correlated with rising temperatures and glacier retreat in the Antarctic (Cabrerizo et al., 2012). Changes in vegetation occurring on the Antarctic Peninsula can be a source of changes in C and N circulation. Cabrerizo et al. (2013) concluded that it can potentially exert a significant influence on POPs circulation through the changing SOM pools. In the context of combined climatic and biogeochemical factors, global change involving different temperatures and organic matter stocks will affect the revolatilisation and reservoirs of POPs (Cabrerizo et al., 2013).

The determination of the exact impact of POPs on Antarctic species and systems, or making forecasts for the future is not yet possible due to the still insufficient number of studies on the Antarctic environment in this aspect. The map of selected POPs (Fig. 5) shows that investigations were focused mainly on the selected parts of Antarctica (South Shetland Islands, Antarctic Peninsula, Victoria Land and Scott Sea), less often they were conducted in the central part of the continent (Vecchiato et al., 2015). However, it is very likely that POPs may be present in the whole Antarctica. Toxic responses to these chemicals, however, have been widely reported in research based on experiments with primarily temperate species under standard test conditions (Bengtson Nash, 2011). It provides the basis for risk assessment for

Fig. 5. Location of research areas in Antarctica, where selected POPs have been determined in biotic and abiotic samples. Abbreviation: TN – total number of researched points, KGI – number of researched points in King George Island, LI – number of researched points in Livingstone Island, VLRS – number of researched points in Victoria Land and Ross Sea, Others – total number of other researched points (prepared based on results obtained by Platt and Mackie, 1980; Subramanian et al., 1983; Bacci et al., 1986; Risebrough et al., 1990; Focardi et al., 1991; Larsson et al., 1992; Caricchia et al., 1995; Kennicutt et al., 1995; Bicego et al., 1996; Fuoco et al., 1996; Inomata et al., 1996; Sen Gupta et al., 1996; Court et al., 1997; Kallenborn et al., 1998; Aislabie et al., 1999; Mazzera et al., 1999; Montone et al., 2001; Corsolini et al., 2002a; Corsolini et al., 2002b; Crockett and White, 2003; Negoita et al., 2003; Montone et al., 2003; Weber and Goerke, 2003; Borghini et al., 2005; Gambaro et al., 2005; Montone et al., 2005; Bustnes et al., 2006; Corsolini et al., 2006; Kim et al., 2006; Negrier et al., 2006; Nemirovskaya, 2006; Corsolini et al., 2007; Curtosi et al., 2007; Krahn et al., 2007; Borghesi et al., 2008; Choi et al., 2008; Cincinelli et al., 2008; Geisz et al., 2008; Klánová et al., 2008; Curtosi et al., 2009; Fuoco et al., 2009; Schiavone et al., 2009a; Schiavone et al., 2009b; Stortini et al., 2009; Taniguchi et al., 2009; Yogui and Sericano, 2009; Cipro et al., 2010; Martins et al., 2010; Park et al., 2010; Corsolini et al., 2011; Van den Brink et al., 2011; Cabrerizo et al., 2012; Fuoco et al., 2012; Li et al., 2012; Trumble et al., 2012; Cabrerizo et al., 2013; Kallenborn et al., 2013; Zhang et al., 2013; Cabrerizo et al., 2014; Lana et al., 2014; Bauner et al., 2015; Jara-Carrasco et al., 2015; Vecchiato et al., 2015; Alexander et al., 2017; Mello et al., 2016; Pongpiachan et al., 2017; the basic maps of Antarctica have been obtained from British Antarctic Survey Geodata Portal, http://add.antarctica.ac.uk/repository/).

Table 2
Examples of negative effects of selected pollutants on living organisms occurring in the Antarctic area.

Contaminants	Species	Observed biological changes	Ref
PAHs	Fish *Notothenia coriiceps*	– Carcinogenic effects on fish; – Damage to liver cells	Curtosi et al., 2009
Hydrocarbons (PAHs, alkanes)	Antarctic sea urchins (*Sterechinus neumayeri*)	– Increased toxic effects immediately following hatching	Alexander et al., 2017
PCBs, HCB, DDT, α-endosulfan, β-endosulfan	Chinstrap penguin (*Pygoscelis antarctica*)	– Decreased reproductive success; – Increased risk of parasitism; – Greater wing asymmetry; – Immunohematological disorders;	Jara-Carrasco et al., 2015
Hg, Pb	Nacella polaris (*Nacella concinna*)	– Disorders of the functioning of gills and muscles; – Inhibitors of arginase activity	de Oliveira et al., 2017
Hg, Cd, Pb	Bald notothen (*Pagothenia borchgrevinki*); Antarctic silverfish (*Pleuragramma antarcticum*); *Notothenia coriiceps*; Emerald rockcod (*Trematomus bernacchii*); *Trematomus hansoni*; *Trematomus newnesi*, *Trematomus pennellii*	– Endocrine disruption; – DNA damage; – Immunotoxicity; – Reprotoxicity	Goutte et al., 2015

high latitude environments. Polar environments have evolved a "boom and bust" ecology governed by seasonal irradiation and primary production (Bengtson Nash, 2011). Moreover, pollutants present in Antarctica may have a number of adverse effects on living organisms, as shown in Table 2. In view of little exposure to POPs and other anthropogenic xenobiotics in the past, the Antarctic organisms probably have not developed detoxification mechanisms like their temperate and tropical counterparts. Sensitivity tests of Antarctic echinoid *Sterechinus neumayeri* on heavy metals showed that its sensitivity was comparable with that of its temperate and tropical counterparts, considering toxicity endpoints at equal exposure durations. Polar organisms, however, are characterised by gigantism as well as slow metabolism and development. Toxicity endpoints can be a good ecological indicator of toxicity comparison only in parallel comparable developmental stages (Bengtson Nash, 2011).

4.1. Pesticides and trace PCBs

Global warming could have a negative effect on the West Antarctic's environment, potentially becoming a net sink of POPs, including pesticides and PCBs (Cabrerizo et al., 2013). Moreover, due to the high storage capacity of soils, the amount of PCBs stored in soils would be up to 74 times higher than in the atmosphere (Cabrerizo et al., 2013). The appearance of relevant sorbing phases at each site (fugacity capacity) in soils of Antarctica can cause better uptake of POPs in Antarctic vegetation. Various factors, including the lipid content, and to a lesser extent age and growth rate, have influence on the accumulation of these compounds in vegetation. The literature provides no information on the age of Antarctic vegetation in the study area. Nonetheless, the organisms are assumed to have been present in the area for a long time, because their growth rate is limited to the environmental conditions which may affect POPs storage.

Mosses and lichens can accumulate and concentrate toxic substances even when POPs are present at low concentrations in the local environment (Cabrerizo et al., 2012). Table 3 shows the concentrations of selected POPs for Antarctic vegetation. POPs concentration values, including PCBs, hexachlorobenzene (HCB), and p,p′-dichlorodiphenyldichloroethylene (p,p′-DDE), determined in tissues of mosses and lichens from the eastern part of Antarctica, range from 0.2 to 34 ng/g dw. In contrast, concentrations of these compounds in mosses and lichens from the western part of Antarctica range from 0.002 to 40 ng/g dw. Microalgae, hair grass, pearl-wort, and green algae are also excellent bioindicators of air pollution of Antarctica (Park et al., 2010; Bacci et al., 1986; Negoita et al., 2003; Cabrerizo et al., 2012; Borghini et al., 2005; Focardi et al., 1991; Montone et al., 2001).

A compared with the range of concentrations of PCBs and pesticides in soils from western Antarctica, concentrations in Antarctic biota have a larger range of concentrations of these compounds (PCB: 0.005–3,86 ng/g dw; HCB: 0.002–2.16 ng/g dw; p,p′-DDE: 0.003–0.60 ng/g dw). In the case of samples from eastern Antarctica, PCB concentrations in Antarctic biota were significantly higher than in soils (soil: 0.005–0.32 ng/g dw; biota: 3.3–34 ng/g dw). HCB concentrations were higher in soils (0.02–25 ng/g dw) than in Antarctic biota

Table 3
Concentration of selected POPs in Antarctic biota.

Sample type	Sampling site/Antarctic sector	ΣPCBs (ng/g dw)	ΣHCB (ng/g dw)	p,p′-DDE (ng/g dw)	Ref
Lichens	King George Island/West Antarctica	0.005–0.04			Park et al., 2010
Lichens	Antarctic Peninsula/West Antarctica		0.32–2.16	0.10–0.60	Bacci et al., 1986
Lichens	Russian stations: Novolazarevskaya, Molodezhnaya, Stornes Peninsula, Progress, Druzhnaya IV and Mirny/East Antarctica	3.3	0.3	0.4	Negoita et al., 2003
Lichens	South Shetland Islands/West Antarctica	0.043–0.61	0.002–0.31	0.003–0.01	Cabrerizo et al., 2012
Mosses	Victoria Land/East Antarctica	23–34	0.85–1.90	1.10–7.90	Borghini et al., 2005
Mosses	Kay Island, Ross Sea/East Antarctica	5–16	0.30–0.80	0.20	Focardi et al., 1991
Mosses	Antarctic Peninsula/West Antarctica		0.30–0.68	0.17–0.53	Bacci et al., 1986
Mosses	South Shetland Islands/West Antarctica	0.04–0.76	0.021–0.12	0.005–0.04	Cabrerizo et al., 2012
Microalgae	King George Island/West Antarctica	0.46–3.86			Montone et al., 2001
Hair grass	South Shetland Islands/West Antarctica	0.39–2.40	0.080–0.20	0.061–0.09	Cabrerizo et al., 2012
Pearl-wort	South Shetland Islands/West Antarctica	0.31	0.04	0.04	Cabrerizo et al., 2012
Green algae	South Shetland Islands/West Antarctica	0.86	0.033	0.08	Cabrerizo et al., 2012
Penguin blood	Lenie Field Station, Admiralty Bay, King George Island/West Antarctica	3.4–9.8	2.7–6.7	4–8.2	Corsolini et al., 2007
Penguin blood	Livingston Island, Kopaitic Island, King George Island/West Antarctica	7.35–8.04	0.79–0.90		Jara-Carrasco et al., 2015
Eggs of seabirds	Admiralty Bay, King George Island/West Antarctica	44.31–1670	118–152		Mello et al., 2016
Tissues of fish	Potter Cove, King George Island/West Antarctica	11.1–99.0		4.59–20.6	Lana et al., 2014

(0.3–1.9 ng/g dw), while the level of p,p'-DDE in soil and Antarctic biota were higher. Some samples of mosses, however, were characterised by a higher content of these pesticides (soil: 0.03–4 ng/g dw; biota: 0.2–7.9 ng/g dw).

An additional factor increasing the risk of POPs accumulation in the tissues of Antarctic organisms are periodic shortages of food and low temperatures (Bengtson Nash, 2011). In conditions of food shortage, lipids are mobilised to satisfy it. This causes a load on contaminants, e.g. POPs contained in lipids. This phenomenon has previously been demonstrated in humans as well as wildlife. The highest vulnerability to the harmful effects of POPs is observed in animal species pushed to physiological extremes through shortage of food, reproduction, or migration, e.g. baleen whales and certain penguin species. It is caused by the re-mobilisation of POPs contained in the adipose tissue and therefore exposure of the body to the toxic effects of these compounds.

4.2. Polycyclic aromatic hydrocarbons and alkanes

Environmental risks regarding the accumulation of PAHs have increased in recent decades due to the growth of anthropogenic emissions from the southern hemisphere (Bargagli, 2008; Xue et al., 2016). Moreover, results showing the capacity for bioaccumulation of PAHs in living organisms, their toxicity, and mutagenity (Yang et al., 2015) demonstrate increased environmental burden of PAHs, particularly in reference to the sensitive Antarctic environment (Cabrerizo et al., 2012). The exposure of PAHs in the Antarctic environment constitutes a threat to Antarctic biota. Mosses are one of the primary components of terrestrial flora in this region. Because they have no root system, they are largely reliant for the nutrients supply on atmospheric deposition (Borghini et al., 2005). PAH accumulation in mosses (Cabrerizo et al., 2012; Colabuono et al., 2015) suggests that Antarctica may become an important sink in the global PAH cycle (Cabrerizo et al., 2012).

Furthermore, Pongpiachan et al. (2017) calculated the quantitative ecological risk assessment of inhabitants exposed to polycyclic aromatic hydrocarbons present in soil samples. The study was conducted on the King George Island, near the Great Wall station in January 2014. The environmental exposure to PAHs for humans in terms of cancer and non-cancer risks was found to be at an "acceptable level".

4.3. Heavy metals and other elements

An increase in human activities in Antarctica, particularly in the "hot spots" near research stations, may further threaten the purity status of the continent if proper precautions are not taken (Lu et al., 2012). At least until the 1990s, no adequate procedures of waste management existed there, leading to the deterioration of the metal pollution situation. As a result of accumulation of progressively adverse effects of different magnitude, the biological, physical, and landscape component of the Antarctic was affected (Chaparro et al., 2007). One of the most noticeable effects of human activity is the accumulation of the trace metals in soils and plant tissues. It has been proven (Amaro et al., 2016) that mercury accumulates more intensively in soils than in mosses. Moreover, the storage of waste causes the emission of chromium and nickel to the soil, where the accumulation of these metals takes place (Abakumov et al., 2017). It has been proved that in Arctic, trace metals are released from permafrost in larger quantities in the summer season, when air temperatures are higher than for the rest of the year (Robinson et al., 2005). Due to the presence of long-term permafrost in Antarctic, the same effect can be assumed to take place. Such a sharp increase in the trace metal load may pose a threat to the environment.

5. Conclusions

Due to prevailing extreme weather, Antarctica provides conditions favourable for permafrost occurrence. According to the available literature, soils of areas free from ice constitute a place of accumulation of heavy metals, PCBs, and PAHs. Due to the sensitivity of permafrost to climate change, the pollution of anthropogenic origin accumulated over the years may be released into the Antarctic environment under the variable conditions. In the context of climate change (depending on the part of Antarctic), either trapping of the compounds (places where cooling is observed/forecasted) or their release can occur (in places of observed/forecasted warming). Moreover, the cycles of accumulation and release of pollutants are also believed to be of seasonal character (winter–summer). Nonetheless, the greatest threat for the environment is posed by pollution reemission. Unfortunately, the literature still provides on information concerning the detailed description of the circulation of pollutants in the Antarctic environment, including the degree of effect of permafrost degradation on pollution remobilisation.

It can be concluded that climate change has become an integral component of research on POPs and heavy metals in Antarctica. These chemical compounds have a negative effect on living organisms occurring in Antarctica, and consequently disturb natural ecosystems in the area. In order to understand the anthropogenic processes and sources of contamination POPs and heavy metals better, their concentration in Antarctica should be constantly monitored. Considering the fact that chemical compounds described in the paper also have their natural sources, there is a need to create indicators of anthropogenic pollution. This would allow to distinguish which of the pollutants are related to human activity, learn about the mechanisms of their migration and limit their emission to the environment. The acquired knowledge can be used in the future for rapid response and environmental renewal in the event of ecological disasters, e.g. oil spills. It will permit limiting the negative impact of humans on the Antarctic environment (e.g. via applying enhanced environmentally friendly solutions), and therefore preserving the environment not only for Antarctic fauna and flora, but also for future generations.

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Publication II is: **Potapowicz J., Lambropoulou D., Nannou C., Kozioł K., Polkowska Ż., Occurrences, sources, and transport of organochlorine pesticides in the aquatic environment of Antarctica, *Science of the Total Environment,* 725 (2020) 139475**. It presents the literature data on organochlorine pesticides (OCPs) occurring in the aquatic environment of both West and East Antarctica. Knowledge about the spatial distribution of these pollutants in waters was explored and information was collected regarding the impact of the presence of OCPs in the environment on living organisms inhabiting the Antarctic area.

The presence of OCPs in the Antarctic region has been attributed to cold condensation and global fractionation during LRAT. Pollutants reach these remote regions of the Earth carried in air masses. This is additionally favoured by the cold-trap effect, which is characterised by the chemical compounds transported in the atmosphere being deposited because of the decrease in temperature when the air masses reach polar regions. The flow of pollutants from melting glaciers also affects the surface water OCP concentrations, and ice can be a vast reservoir of OCPs. It has been observed that snow can be a seasonal secondary source.

It was found that OCPs that are present in Antarctic waters and biota constitute a threat to the proper functioning of aquatic organisms. This is undoubtedly favoured by these chemical compounds having a long residence time in the Antarctic environment and thus persisting even after a long period following emission. Due to their properties, OCPs degrade slowly and have the ability to accumulate in the Antarctic environment. The most commonly detected OCPs in the Antarctic environment are dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), aldrin, dieldrin, endrin, isodrin and chlordanes. In addition, chemicals from this group have been identified in various aquatic environments of the Antarctic (seawater and polynya water, freshwater, porewater, snow, firn and ice). Regarding biota, the presence of OCPs in multiple tissues of aquatic organisms, bird eggs, and the contents of the digestive tract of animals at higher trophic levels was found. OCPs and their degradation products alike negatively affect the living organisms in Antarctica, disrupting the natural ecosystem. Their presence in tissues may cause, among other

things, reproductive disorders, increased parasitic load, increased asymmetry of wings, and immune-haematological disorders. Detailed analysis of the literature allowed for the selection of these groups of pollutants for further research under the project “Preludium 19” funded by the National Science Centre entitled “Determination and characteristics of pollution release due to climate change from glaciers and snow melting in Antarctica”, of which I am the principal investigator.

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Review

Occurrences, sources, and transport of organochlorine pesticides in the aquatic environment of Antarctica

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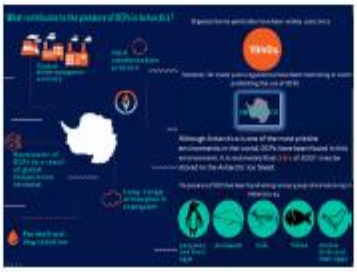
HIGHLIGHTS

- OCPs in the Antarctic come from distant anthropogenic activity.
- Melting ice plays an important role in the fate of OCPs in the Antarctic environment.
- The presence of OCPs causes multiple negative effects on Antarctic fauna.

GRAPHICAL ABSTRACT



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Antarctica

ABSTRACT

We review information on the concentration levels of organochlorine pesticides in the abiotic aquatic environment (in seawater, sea ice, surface freshwater, snow, firn, and glacial ice) and the organisms inhabiting those, in Antarctica. Particular attention is given to the environmental fate of these pollutants, which modifies their impact on the organisms living in the Antarctic. OCPs have been delivered to the Antarctic environment mainly via long-range transport from inhabited areas, and due to their long accumulation they are sometimes reemitted from melting cryosphere. Since climate change is forecasted to intensify, the release of anthropogenic pollutants from increased seasonal thaw may prove its importance for the future state of this unspoiled environment. However, the limited estimations of the OCPs storage magnitude in the Antarctic cryosphere are relatively crude and may err significantly towards higher values. The OCPs are already present in different types of animal tissues at every trophic level, where they may cause negative effects such as reproductive disorders, decreased survival rates, and an increased parasitic load. Therefore, it is important to continuously monitor OCP concentrations in various elements of the Antarctic environment and the fate of these pollutants, taking into account their global and local sources, including the remobilization from frozen state.

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Contents

1. Introduction

The ecosystem in Antarctic waters is uniquely adapted (Cavicchioli, 2015) and globally relevant for primary productivity (Dierssen et al., 2000). While Antarctica is one of the most pristine environments in the world (Ainley, 2007), the aquatic organism there is still exposed to pollution. The effects of human activities can be observed in the Antarctic environment (Gao et al., 2018; Geisz et al., 2008; Tanabe et al., 1983), such as the footprint of tourist and research station activities (Szopińska et al., 2018; Harcha, 2006). In the recent decades, there has been a rapid increase in global pollutant emissions in general, which contributed to their distribution across the global environment (Cipro et al., 2013; Yadav et al., 2017; Ma et al., 2017; Potapowicz et al., 2019). Unfortunately, this global trend affects even the Antarctic environment, requiring more and more of the global scientific community (Möller et al., 2012; Cincinelli et al., 2016; Vecchiato et al., 2015). As a result of the global anthropogenic activities, an accelerated warming and other climatic changes have been observed in the Antarctic (Kejna et al., 2013; Szopińska et al., 2018). As a result of these changes, an increased transport of pollutants from urban areas due to air mass movement was observed (Corsolini, 2009; Bengtson Nash, 2011) and reemission of pollutants from permafrost to the Antarctic environment has also been considered in this area (Szopińska et al., 2018). The most frequently raised issue by scientists is the increase in trace metals concentrations in this area (e.g. Abakumov et al., 2017; Lu et al., 2012; Santos et al., 2005; Szopińska et al., 2018; Tin et al., 2009). It was found that the concentrations of persistent organic pollutants (POPs) increase in biological tissues collected in Antarctica.

A particularly long-standing threat among the POP compounds detected in Antarctica is organochlorine pesticides (OCPs) (Cipro et al., 2017; Bigot et al., 2016a). Since the 1940s, these compounds have been widely used, mainly in agriculture. However, for many years, regulations have been restricting or even prohibiting the use of OCPs. One of them is the Stockholm Convention, adopted by the United Nations Environment Program. Legislation largely protects the environment against increased OCPs in the environment, but not all countries comply with these bans. In addition, OCPs are resistant to environmental degradation processes (Bigot et al., 2016b).

In general, OCPs have been transported from populated areas to the Antarctic by long-range atmospheric transport (LRAT), where their further movement has been restricted by the cold conditions (Bigot et al., 2016b; Geisz et al., 2008). As a result, OCPs were deposited in snow and ice; afterwards, melting, especially the release of particulate organic matter from the ice, feeds them into the base of the food web (yet a proportion of the released OCPs may come back to the atmosphere through volatilisation) (Chiuchiolo et al., 2004). During circumpolar long-term research in the Antarctic over the last several decades, climate change and the resulting melting and retreat of Antarctic ice shelves was observed (Vaughan et al., 2003; Turner et al., 2005; Mulvaney et al., 2012; Kejna et al., 2013). Ducklow et al. (2007) showed that regional climate warming correlates with ecosystem changes throughout the sea-ice dominated areas of the Western Antarctic Peninsula. In addition, Bogdal et al. (2009) have observed (in the European Alps) that pollutants may be secondarily input to the environment through glacier melt, while Bigot et al., 2016b confirmed their presence in Antarctic ice cores. Particularly noteworthy is the fact that it may come to the possible future reemission of OCPs, among other POPs, into the atmosphere and surface waters. These chemical compounds have accumulated in the Antarctic over the years in the ice layers corresponding to the pollutant emission period.

OCPs, considered the typical persistent toxic substances (PTS), deserve special attention because of their persistence, bioaccumulation, and toxicity (Chopra et al., 2011; Willett et al., 1998; Quan et al., 2003; Wong et al., 2004). The presence of OCPs in the Antarctic environment was reported for the first time in the 1960s (Sladen et al., 1966; George and Frear, 1966). In the 12th Stockholm Convention, eleven OCPs were proposed to be controlled because of their harmful effects to the environment and ecosystems (Chopra et al., 2011; Bigot et al., 2016b), including dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), pentachlorobenzene, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene, hexachlorocyclohexane (alpha-HCH, beta-HCH, and gamma-HCH, also named lindane), and chlordecone, while endosulfan has recently been proposed to the European Union to be included under the provisions of the above-mentioned Convention. Despite the introduction of bans and restrictions on the use of OCPs, many research groups showed that these compounds occur both in the Antarctic aquatic environment and in the trophic networks of organisms living in this area (Chiuchiolo et al., 2004; Dickhut et al., 2005; Inomata et al., 1996; Sun et al., 2006; Taniguchi et al., 2009; van den Brink, 1997).

The toxic effects of OCPs on biota are known, as detailed in publications on the areas with more intensive human activity (Agnihotri et al., 1994; Bai et al., 2018; Barhoumi et al., 2014; Carlson et al., 2004; Carro et al., 2017; Petrovic et al., 2018). In the case of ecosystems found in Antarctica, the fate of these compounds is also affected by the low temperature conditions (Zhang et al., 2013). Lipophilic OCPs accumulate in the fat tissue of biological organisms and can be biomagnified, which poses a risk to organisms of higher trophic levels. For example, Jara-Carrasco et al. (2015) proved that significant concentrations of HCB, DDT, α-endosulfan, β-endosulfan in tissues of Chinstrap penguin (*Pygoscelis antarctica*) can result in adverse changes, such as decreased reproductive success, increased risk of parasitism, greater wing asymmetry and immunohematological disorders. There are many studies regarding OCPs concentration levels in penguin and pinniped mammals' tissues, as well as on the impact of these compounds on life processes (George and Frear, 1966; Schiavone et al., 2009; Sun et al., 2006). Research on the determination of OCPs in aquatic organisms that are at the beginning of the trophic chain, e.g. the Antarctic krill, is also warranted by their multiplied impact on the higher trophic levels (Cipro et al., 2013; Goerke et al., 2004).

Considering that OCPs are bioaccumulated in the tissues of living organisms at different trophic levels, it is important to compare the concentrations of these chemical compounds in various animal tissues, as well as to determine the impact of OCPs on the Antarctic biota. This work is an attempt to compile the existing knowledge on the status of these chemicals in the aquatic environment of the Antarctic, taking

into account both the abiotic background concentrations and the aquatic or semi-aquatic animals. While the comparison of OCP concentrations in these two elements of the Antarctic environment has been missing in the previous work, it may be important for understanding the exchange of these compounds to and from the Antarctic ecosystem, and learning about the processes occurring in this polar environment. Special attention has been paid to the different sources of these compounds (anthropogenic, local or long-distance) and the environmental fate of pollutants. The proposed review will also contribute to assessments of the potential environmental hazards associated with the accumulation of OCPs in the Antarctic environment.

2. Sources and the deposition of organochlorine pesticides in Antarctica

Organochlorine pesticides are widespread contaminants in many environments around the world, including the polar regions. Studies over the years have shown that OCPs are detected in the Antarctic air (Kang et al., 2012), water (Cipro et al., 2017), soil (Zhang et al., 2015) and biota (Schiavone et al., 2009). The presence of OCPs in this region has been attributed to cold condensation and global fractionation during the long-range atmospheric transport (LRAT) (Wania and Mackay, 1996). In addition, local impact on the increase of environmental pollution in latitudes over 62°S is also observed (Evenset et al., 2007; Roosens et al., 2007).

In a description of the environmental fate of OCPs in polar environments, one cannot ignore the impact of the cold trap effect. This phenomenon is characterized by the transport of chemical compounds in the atmosphere, caused by a decrease in temperature and resulting in the deposition of these compounds. It has been shown that despite the highest POPs emission at temperate and tropical temperatures, these pollutants do not remain there; a proportion of their chemical load volatilizes and then moves through the atmosphere, to be later condensed at colder, higher latitudes (Wania and Mackay, 1993, 1996; Dickhut et al., 2005). Cycles of long-range atmospheric transport, deposition and reemission (Rappe, 1974; Goldberg, 1975) can be repeated many times which makes them a source of pollution in areas with insignificant anthropogenic activity, such as Antarctica, leading to the accumulation of these compounds (Wania and Mackay, 1993, 1996; Jones and De Voogt, 1999). The transport of pollutants in the atmosphere has a significant impact on the pollution load in the hydrosphere (Bidleman, 1999). In addition, Galbán-Malagón et al. (2013) showed that in the Antarctic environment, the biological degradative processes in water may result in disequilibrium in atmospheric and aquatic concentrations of OCPs, driving the absorption of HCHs and HCB through air-to-water fluxes.

One of the important aspects affecting the presence and spread of OCPs in polar environments is global climate change. These processes affect the transport and redistribution pathways of POPs (Kallenborn et al., 2012; Kosek et al., 2018). It is caused by the dependence accumulation, reactivity and adsorption processes are temperature dependent (Kallenborn et al., 2012). Glaciers are an important component of the Antarctic and Arctic regulating water circulation in the cold environments. They are characterized by the fastest and strongest respond to climate changes (Lehmann et al., 2016). Global warming can cause the release of accumulated quantities of OCPs in glacial ice, which will result in the increase the loading of these pollutants in glacial-fed systems (Weber et al., 2010). Many physical and chemical properties of POPs provide information regarding their presence and distribution in the environment (Kosek et al., 2018). In addition, the values of some of them, e.g. a chemical's vapor pressure, Henry's law constant, the air-water partitioning coefficient and the octanol-air partitioning coefficient are related to the temperature value (Kallenborn et al., 2012). While seasonal changes in air temperature do not drastically affect the properties of chemical pollutants, so many years of climate change over the decades can contribute to drive phase partitioning of semi-volatile chemicals towards the gas phase (Kallenborn et al., 2012). The consequence of this may be an increase in the translocation of chemical compounds in the environment, thereby increasing the extent of pollution.

It has been observed that snow can be a seasonal secondary source (Fig. 1) of OCPs in Antarctica (Kallenborn et al., 2013). This phenomenon is particularly relevant to lighter and more hydrophilic compounds

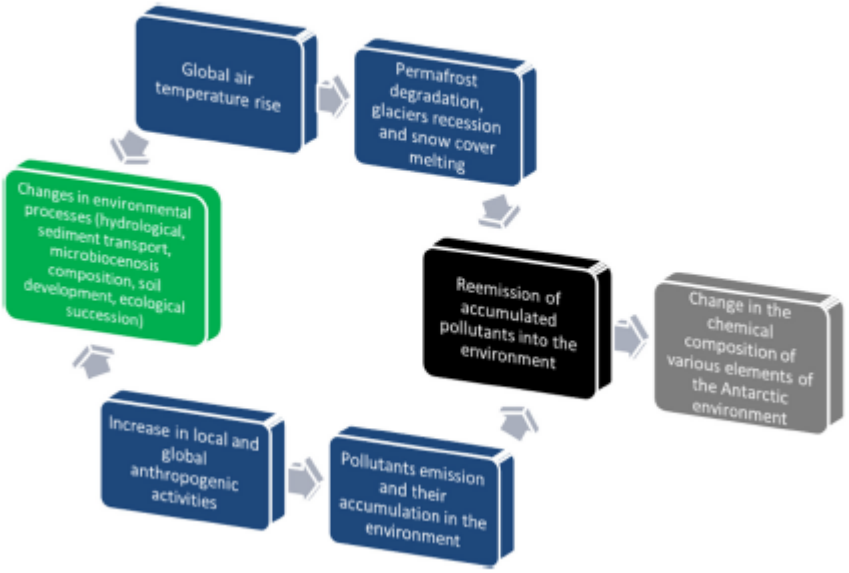

Fig. 1. A diagram of the secondary release of OCPs in Antarctica.

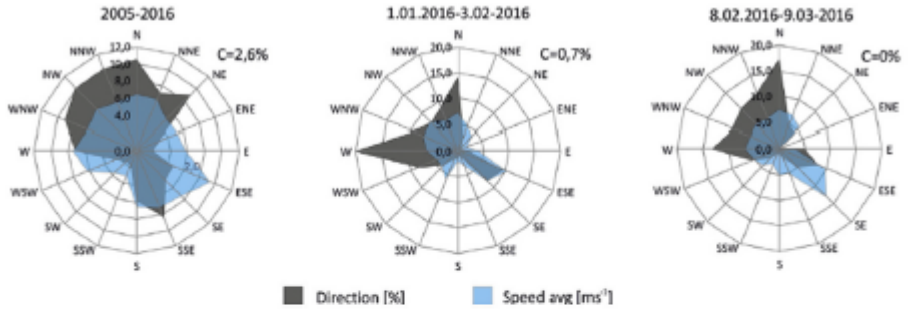

Fig. 2. Wind directions and wind speed in the period of 2005–2016 at the Bellingshausen Station (King George Island, Maritime Antarctica) (Szopińska et al., 2018).

(Muir and Lohmann, 2013). Falling snow removes OCPs from the atmosphere through washout of atmospheric aerosols and absorption of their vapors (Kang et al., 2012). Therefore, the accumulation of these compounds in the environment is promoted, affecting their further fate (Daly and Wania, 2004; Stocker et al., 2007). Despite their lipophilic nature, OCPs are accumulated in the snow and ice, constituting a reservoir of these compounds. Due to their lipophilic character, on the other hand, they are capable of bioaccumulation and further adverse effects on fauna (Chopra et al., 2011; Geisz et al., 2008). During their research, Cipro et al. (2017) observed that as the general sum of the OCP concentrations decreases during the austral summer season, proportionally the concentrations in snow remain higher than in snow meltwater. This can be caused by the non-linear redistribution of the compounds between these two phases (Gross et al., 1977). In addition, OCPs may enter a new state of equilibrium, reevaporate or be adsorbed to organic matter after entering the liquid phase (Wania, 1997).

The flow of pollutants from melting glaciers also affects the surface water OCP concentrations (Blais et al., 2001; Li-guang et al., 2005), and ice can be a vast reservoir of OCPs. It is estimated that 3.6 t of ΣDDT may be stored in the "Antarctic Peninsula ice sheet" (Geisz et al., 2008), yet the estimation seems to apply the average concentration of the pollutant in the top 6 m of snow to the whole ice sheet thickness (averaged as 1780 m), which is an obvious misrepresentation of the period when this contaminant was deposited. Thus, most likely, the storage of the pollutant in the ice sheet has been much lower than estimated. It should also be decreasing where glaciers experience surface ablation. Ducklow et al. (2007) noticed a 6 °C-increase in the mean winter temperature, while the annual mean temperature increased by 2 °C on the Antarctic Peninsula from 1950. In addition, the ice volume loss, glacier retreat and meltwater production have also increased (Cook et al., 2005). The conditions described are conducive to the release of pollutants accumulated in ice, which is confirmed by research on the concentrations of selected compounds in glacial runoff (Chiuchiolo et al., 2004).

It is believed that the inflow of pollutants to the Antarctic Peninsula is strongly limited by the range of circumpolar air circulation (Szopińska et al., 2018), yet small concentrations of pollutants are delivered to the interior of Antarctica. The redistribution of such pollutants is affected, among other factors, by wind speed and direction. Mishra et al. (2004) drew attention to the long-range atmospheric transport of metallic compounds identified in the air at the King Sejong Station (King George Island, South Shetlands Islands). In addition, Kallenborn et al. (2013) observed the same effect in the case of POPs on Dronning Maud Land, and Lee et al., 2004 with reference to volcanic ashes from Patagonia in the soil of the Barton Peninsula. Szopińska et al. (2018) analyzed the wind directions at King George Island in 2016, based on the data from Bellingshausen station. The authors concluded that predominant wind directions are north-westerly (30% - NNW, NW, WNW) northerly (10% - N), north-easterly (9% - NE) and south-easterly (8% - SSE). Furthermore, it was observed that the dominant wind direction also changes depending on the season (Fig. 2).

The Southern Hemisphere atmospheric circulation transports pollutants from populated emission areas to the Antarctic, where they are deposited (Russell and McGregor, 2010), e.g. with snow, and remain due to cold condensation (Wania and Mackay, 1993). While the degree of pollution in the Antarctic Peninsula may have a direct connection to Argentina and Chile (Dickhut et al., 2005), in remote regions of Antarctica it has been suggested that a potential secondary source can be also the wind ventilation of snow (Kang et al., 2012). However, as the air masses travel a long way into the Antarctic continent, their pollutant load becomes more diluted in the atmospheric air and, consequently, the inland areas experience lower levels of OCPs in snow than the Antarctic coast (Kang et al., 2012). Bigot et al. (2016a), who compared OCP concentrations in air and seawater at points located across the Southern Ocean, also found them diminishing with increasing latitude. Finally, local orographic conditions modify the level of contamination (Kejna et al., 2013).

3. Levels of organochlorine pesticides in the aquatic environment and fauna in Antarctica

OCPs have been found even in as pristine an environment as Antarctica. Table 1 presents the published data on the concentrations of selected OCPs in the aqueous abiotic environment of Antarctica in relation to geographical location, type of matrix (water, snow, ice), water salinity (seawater and freshwater) and sampling year.

In the water and snow all the determined compounds from the OCP group chosen for this review were found, i.e. dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), drins (aldrin, dieldrin, endrin and isodrin), chlordanes (α- and γ-chlordane, oxychlordane, heptachlor epoxide). Ice samples were characterized by significant concentrations of HCHs and chlordanes (Dickhut et al., 2005). DDTs and HCHs were the most common OCPs in all environmental samples. Based on the literature (Table 1), it can be concluded that the concentration levels of selected OCPs in various elements of the Antarctic environment were relatively low (usually at 1–600 pg/L level), most likely due to the large distance from densely populated areas and the geographical barrier (the ice barrier of Antarctica) hindering the transport of pollutants. In addition, Fig. 3 shows the location of research areas in Antarctica, where selected OCPs have been determined in water, ice and snow.

In the case of freshwater, the highest concentrations of DDTs, chlordanes and drins were found in waters originating from a lake on King George Island (Gao et al., 2018). ∑OCPs in this lake water reached concentrations of to 0.33 ng/L in one sample. The authors claim that such high concentrations of OCPs there result from the relative proximity of lower latitude emission areas. This explanation aligns with the observation of Bigot et al. (2016a), that the concentration of some OCPs in the

Table 1
The total dissolved concentrations of OCPs in water, snow, and ice, at various sampling sites.

Type of sample	Location	DDTs[a]	HCHs[b]	HCB	Drins[c]	Chlordanes[d]	Unit	Reference
Freshwater	Lake Nurume	1.3	330	–	–	–	pg/L	(Tanabe et al., 1983)
	Brazilian Research Station Feraz, King George Island	4.32–6.30	2.06–3.14	1.76–2.47	<0.35–2.73	5.72–7.48	pg/kg	(Cipro et al., 2017)
	Lake on King George Island	<LOD–0.073	–	–	<LOD–0.11	<LOD–0.33	ng/L	(Gao et al., 2018)
Polynya water	Dakshin Gangotri	24.8–26.5	85.6–90.7	–	–	–	pg/L	(Sen Gupta et al., 1996)
Seawater	Western Ross Sea	–	0.61–8.79	1.72–16.24	–	–	pg/L	(Cincinelli et al., 2009)
	Tottuki Point	1.3	570	–	–	–	pg/L	(Tanabe et al., 1983)
	Langhovde	1.5	210	–	–	–		
	Kitano-ura Cove	1.5	570	–	–	–		
	Southern Ocean (Weddell, South Scotia, and Bellingshausen Seas)	–	0.189 ± 0.09–3.132 ± 4.031	0.281 ± 0.078–0.976 ± 0.828	–	–	pg/L	(Galbán-Malagón et al., 2013)
	Dakshin Gangotri	0.63–4.27	–	–	–	–	pg/L	(Sen Gupta et al., 1996)
	King George Island	<LOD–0.044	–	–	<LOD–0.42	<LOD–0.49	ng/L	(Gao et al., 2018)
	Palmer Station	–	2.7–15.04	–		–	pg/L	(Dickhut et al., 2005)
	Southern Ocean	0.59–5.61	<2.96–7.67	2.59–4.14	<0.65–1.43	<0.17–0.44	pg/L	(Bigot et al., 2016a)
Snow	Dome Fuji, East Antarctica	–	17.5–137.0	<LOD–18.2	–	–	pg/L	(Kang et al., 2012)
	Mizuho Station	15	2300	–	–	–	pg/L	(Tanabe et al., 1983)
	Tottuki Point	17	2800	–	–	–		
	Lake Nurume	16	4900	–	–	–		
	Brazilian Research Station Feraz, King George Island	5.3–24.4	1.46–4.17	1.36–3.77	<0.35–4.29	11.39–13.3	pg/kg	(Cipro et al., 2017)
	Palmer Station	–	3.17–8.91	–	–	<LOD–7.82	pg/L	(Dickhut et al., 2005)
Ice cover	Tottuki Point	11	2200	–	–	–	pg/L	(Tanabe et al., 1983)
	Lake Nurume	9.8	2000	–	–	–		
Sea-ice	Palmer Station	–	5.24–7.46	–	–	<LOD–8.02	pg/L	(Dickhut et al., 2005)
Porewater in sediments	Western Antarctic Peninsula	0.11–1.00	–	0.63–6.7	–	–	pg/L	(Zhang et al., 2013)

LOD - limit of detection.
[a] DDTs: p,p′-DDE; o,p′-DDT; p,p′-DDD; p,p′-DDT.
[b] HCHs: α-HCH; β-HCH; γ-HCH.
[c] Drins: aldrin, dieldrin, endrin and isodrin.
[d] Chlordanes: α- and γ-chlordane, oxychlordane, heptachlor, and heptachlor epoxide.

oceans decreased with latitude. Furthermore, in the King George Island area, the lake water concentration of DDTs, chlordanes and drins exceeded those in seawater. This fact may be explained by a continuous accumulation of pollution in the lake without drainage and the slow processes of neutralising such pollution. In particular, the extra load of organochlorine pollutants entering the lakes (and the sea, in a more dilute form) may come in the cold climate from melting snow and ice covers (Cabrerizo et al., 2019). As for HCHs in freshwater, their highest concentration levels were found at Lake Nurume near Syowa Station (Tanabe et al., 1983). The station is located on East Ongul Island in Queen Maud Land, Antarctica. The authors claimed that the source of DDT and HCH was in the developing countries in the tropics (via long-range transport), which at the time used these pesticides in large quantities. In addition, Lake Nurume is located at a relatively low latitude, which increases the pollution inflow.

The concentrations of OCPs in seawater are typically lower than in freshwater, yet this pattern did not occur for HCHs near Syowa Station (Tottuki Point, Kitano-ura Cove) (Tanabe et al., 1983) and HCB in the western Ross Sea (Cincinelli et al., 2009) and in the Southern Ocean (Bigot et al., 2016a). These points are located on opposite ends of the Antarctic. Cincinelli et al., 2009 stated that the high OCPs concentrations may result from their inflow from melting sea ice and snow, and the decrease in HCB in the spring may be the result of bioaccumulation in phytoplankton, as well as to volatilisation due to HCB high vapor pressure. The latter explanation appears more likely, as Chiuchiolo et al. (2004) report no bioaccumulation or biomagnification of HCB at the lowest levels of the Antarctic food web (ice algae and krill).

In snow and ice, the concentrations of selected OCPs are higher than in freshwater and seawater. However, polynya water (Sen Gupta et al., 1996) exhibited notably higher concentrations than seawater in general, as well as sea ice (Dickhut et al., 2005), and effect which Pučko et al. (2015) attribute to enhanced dry deposition of OCPs in these melt ponds. Particularly noteworthy are again snow and ice samples taken near Syowa Station (Tanabe et al., 1983), which were characterized by many times higher HCHs concentrations than in other places in Antarctica. For these and other matrices, the high concentrations may be connected to the year when the samples were collected. Since then, the use of OCPs has been significantly reduced due to their harmful environmental impacts. The highest concentrations of DDTs, drins and chlordanes in snow and ice were found in the King George Island area, near Brazilian Research Station Feraz (Cipro et al., 2017). The authors point out the possible cause of differences in OCP concentrations between water and snow/ice, which is that during melt this class of pesticides can be lost through volatilisation or adsorption on organic matter. Furthermore, their elution pattern during snow melt may concentrate them at certain times, as opposed to relative dilution at other – e.g. for lindane (γ-HCH), the concentration is enhanced at the beginning and the very end of snow melt (Meyer and Wania, 2011).

Table 2 presents a literature review of the concentrations of selected OCPs in Antarctic biota, with respect to the type of sampled tissue, sample collection year, animal species, and trophic level. Fig. 3 shows the spatial distribution of research areas, where selected OCPs have been determined in Antarctic fauna. The highest concentrations of DDTs and endosulfans were found in penguin blood, in samples from Kopaitic

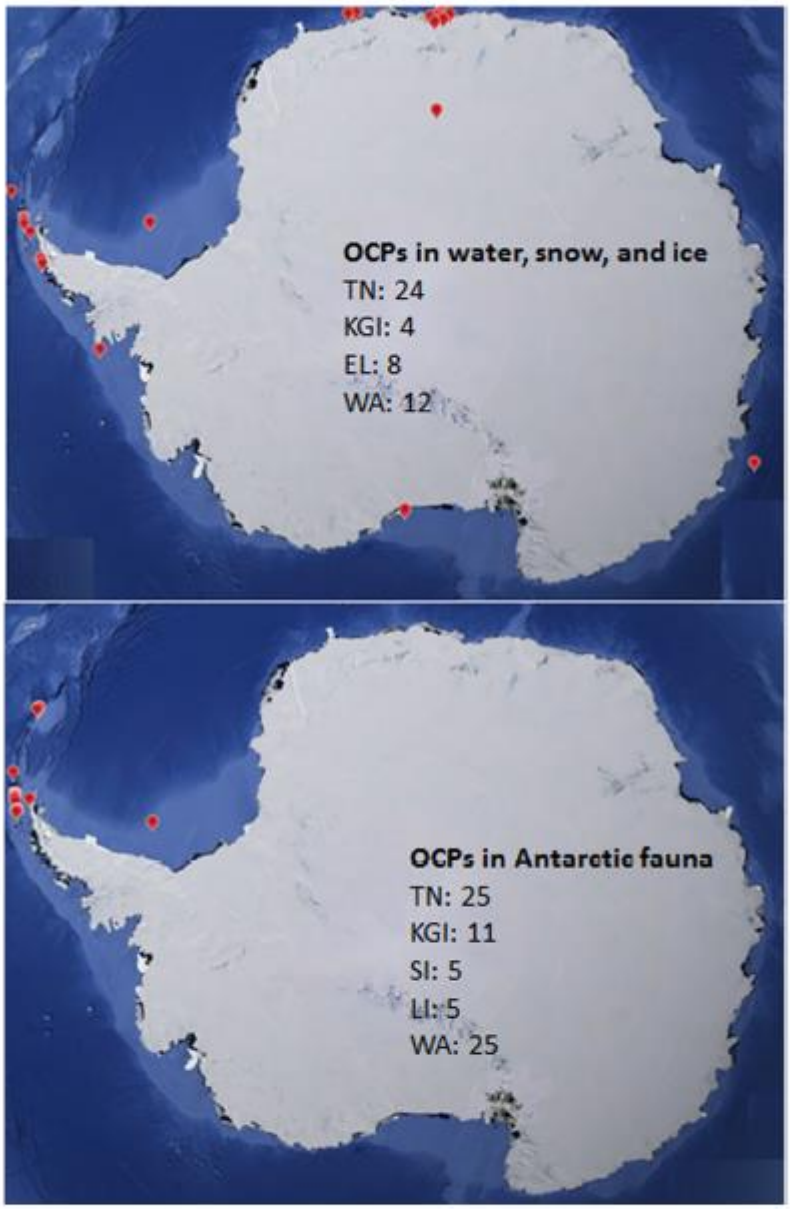

Fig. 3. Location of research areas in Antarctica, where selected OCPs have been determined in aquatic and biotic samples. Abbreviation: TN – total number of researched points, KGI – number of researched points in King George Island, LI – number of researched points in Livingstone Island, EL – number of researched points in Enderby Land, EL – number of researched points in Signy Island, WA – number of researched points in western Antarctica. Maps have been prepared based on results obtained by articles in Tables 1 and 2.
The maps were made using https://earth.google.com/.

Island and in the area of Cape Shirreff, respectively (Jara-Carrasco et al., 2015). The highest level of HCB concentration was found in the area of Lenie Field Station on King George Island (Corsolini et al., 2007). Jara-Carrasco et al. (2015) showed that differences in the concentration of selected OCPs in the blood of individual species of penguins may be due to the differences in their diet and their migration behaviour exposing them to varying concentrations of these pollutants at different times of the year. Furthermore, it has been suggested that the presence of

Table 2
The concentrations of OCPs in Antarctic fauna at different sampling sites.

Type of sample	Localization	Tissue type and animal species	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
Penguin tissues	Brazilian Research Station Feraz, King George Island	Penguins (Adelie penguin, Papua penguin and Gentoo penguin) fat	370	12.3	373	26.4	–	73.5	ng/g lipid weight	(Taniguchi et al., 2009)
	Signy Island	Adélie penguin liver	0.002–0.028	–	–	–	–	–	μg/g	(Tatton and Ruzicka, 1967)
		Adélie penguin blubber	0.013–0.054	–	–	–	–	–		
		Adélie penguin abdominal fat	0.035–0.059	–	–	–	–	–		
	Lenie Field Station, King George Island	Adélie penguin blood	–	–	5–7.4	–	–	–	ng/g wet weight	(Corsolini et al., 2007)
		Chinstrap penguin blood	–	–	0.001–9	–	–	–		
		Gentoo penguin blood	–	–	2.8–4.9	–	–	–		
	Cape Shirreff	Chinstrap penguin blood	6.90	–	0.79	–	7.72	–	ng/g wet weight	(Jara-Carrasco et al., 2015)
	Kopaitic Island	Chinstrap penguin blood	7.34	–	0.85	–	3.98	–		
	Naephiki Point	Chinstrap penguin blood	3.19	–	0.90	–	5.50	–		
Penguin eggs	Livingstone Island	Adélie penguin eggs	23 ± 10	–	7.63 ± 1.8	–	–	–	ng/g wet weight	(Schiavone et al., 2009)
		Chinstrap penguin eggs	17 ± 15	–	3.8 ± 3.7	–	–	–		
		Gentoo penguin eggs	15 ± 9	–	3.7 ± 3.5	–	–	–		
	Signy Island	Adélie penguin eggs	0.019–0.044	–	–	0.003–0.008	–	<1.00	μg/g	(Tatton and Ruzicka, 1967)
	Polish Antarctic Station Arctowski, King George Island	Adélie penguin eggs	49.6–137	–	110–208	–	–	–	ng/g lipid weight	(Mello et al., 2016)
	Chabrier Rock, King George Island	Chinstrap penguin eggs	62.5–338	–	70.1–191	–	–	–		
	Lenie Field Station, King George Island	Gentoo penguin eggs	36.4–120	–	110–183	–	–	–		
Other bird tissues	Brazilian	Brown skua fat	11,958	1.22–3.11	573	2.54	–	13.85	ng/g lipid weight	(Taniguchi et al., 2009)
	Research Station Feraz, King George Island	Antarctic tern fat	1001	<0.12–2.60	601	<0.48–23.0	–	124.8		
		Blue-eyed shag fat	746	1.33	161	<0.48	–	3.05		
		Snowy sheathbill fat	909	<0.12	282	22.4		179.3		
	Signy Island	Brown skua liver	1.12–4.33	–	–	<1.00	–	0.035–0.1	μg/g	(Tatton and Ruzicka, 1967)
		Brown skua fat	6.69–28.50	–	–	<1.00	–	0.120–0.730		
		Blue-eyed shag fat	0.063–0.163	–	–	0.004–0.006	–	<1.00		
Other bird eggs	Punta Hennequin, King George Island	South polar skua eggs	222–4570	–	20.5–224	–	–	–	ng/g lipid weight	(Mello et al., 2016)
Pinniped tissues	Livingstone Island	Antarctic fur seal (*Arctocephalus gazella*) blubber	<1.00	–	<1.00	–	–	–	ng/g wet weight	(Schiavone et al., 2009)
		Antarctic fur seal (*Arctocephalus gazella*) liver	191 ± 106	–	2.2 ± 0.88	–	–	–		
		Antarctic fur seal (*Arctocephalus gazella*) muscle	103 ± 55	–	1.37 ± 0.69	–	–	–		
	King George Island	Crabeater seal (*Lobodon carcinophagus*) fat	14.4	0.223	7.23	18.4	2.09	22.8	ng/g lipid weight	(Ciprot et al., 2012)
		Antarctic fur seal (*Arctocephalus gazella*) fat	168	3.21	4.72	82.4	21.15	78.2		
		Weddell seal (*Leptonychotes weddellii*) fat	131	2.59	5.77	18.5	14.0	9.5		
		Southern elephant seal (*Mirounga leonine*) liver	98.7	1.41	7.48	6.88	2.72	37.7		

(continued on next page)

Table 2 (continued)

Type of sample	Localization	Tissue type and animal species	DDTs[a]	HCHs[b]	HCB	Drins[c]	Endosulfan[d]	Chlordanes[e]	Units	Reference
	Elephant Island	Southern elephant seal	187.72	1.905	9.89	10.205	2.85	37.28	ng/g lipid weight	(Miranda-Filho et al., 2007)
	Cape Shirreff Field Station	Antarctic fur seal (*Arctocephalus gazella*) blubber	5.66	44.27	109.59	10.77	7.01	45.60	ng/g lipid weight	(Vergara et al., 2019)
		Southern elephant seal blubber	<LOD	19.88	12.88	26.08	0.76	6.71		
	Cape Shirreff Field Station and Gabriel Gonzalez Videal Station	Weddell seal (*Leptonychotes weddellii*) blubber	7.6–17.81	48.96–75.41	94.57–340.66	34.72–42.13	0.70–3.88	37.87–106.17		
		Leopard seal blubber	5.51–7.29	49.75–76.07	81.15–95.45	15.01–31.18	0.12–4.65	35.65–62.88		
		Crabeater seal (*Lobodon carcinophagus*) blubber	<LOD	75.70–111.15	72.86–311.39	14.76–61.60	<LOD-3.72	50.10–52.66		
Aquatic organisms tissues	Signy Island	Notothenia - fish	0.008–0.033	–	–	0.001–0.009	–	0.002–0.004	μg/g	(Tatton and Ruzicka, 1967)
	Potter Cove, King George Island	*Notothenia coriiceps* (mean in muscle, liver, gonads, gills) - fish	11.9 (muscle); 14.7 (liver); 13.3 (gonads); 14.3 (gills)	3.40 (muscle); 1.29 (liver); 18.0 (gonads); 9.21 (gills)	–	–	–	–	ng/g lipid weight	(Lana et al., 2014)
		Notothenia rossii (sum in muscle, liver, gonads, gills) - fish	253.6	49.03	–	–	–	–		
		Trematomus newnesi (sum in muscle, liver, gonads, gills) - fish	54.2	31.9	–	–	–	–		
	Weddell Sea	*Chionodraco hamatus*	12	0.94	7.9	–	–	–	ng/g lipid weight	(Strobel et al., 2018)
		Trematomus loennbergii	2.9	4.83	3.1	–	–	–		
	King George Island	Nacella concinna soft tissue	<LOD–1.27	1.6–3.19	<LOD–8.56	<LOD–1.11	<LOD	2.37–3.94	ng/g wet weight	(Ciprotti et al., 2013)
		Euphausia superba	0.05–0.79	0.14–0.35	<LOD – 0.06	<LOD–0.44	<LOD	<LOD–0.13		
		Notothenia spp. muscle	<LOD–11.7	<LOD–0.57	<LOD–0.06	<LOD	<LOD–0.203	<LOD–1.49		
Other	Adley Island	Gentoo penguin droppings	1.49	2.67	–	–	–	–	ng/g	(Sun et al., 2006)
	Signy Island	Adélie penguin stomach contents	0.001	–	–	0.001	–	<LOD	μg/g	(Tatton and Ruzicka, 1967)

LOD - limit of detection.
[a] DDTs: p,p′-DDE; o,p′-DDT; p,p′-DDD; p,p′-DDT.
[b] HCHs: α-HCH; β-HCH; γ-HCH.
[c] Drins: aldrin, dieldrin, endrin and isodrin.
[d] Endosulfans: α-endosulfan; β-endosulfan.
[e] Chlordanes: α- and γ-chlordane, oxychlordane, heptachlor, and heptachlor epoxide.

endosulfans in Antarctica can be caused by the intensive use of insecticide in South America, especially in Argentina (Pérez et al., 2013). Both the production and the use of this insecticide have been banned relatively recently, in July 2013. Finally, attention should be paid to the geographical location of the points with the highest concentration of OCPs in penguin blood. These were all located in the vicinity of South Shetland Islands or South Orkney Islands. These islands are exposed to the largest inflow of pollution from densely populated areas.

OCPs have also been found in penguin fat and liver. Tatton and Ruzicka, 1967 wrote about DDTs content in tissues at the level of 0.002–0.059 mg/kg, which represents a low concentration compared to the study of Taniguchi et al., 2009, who found concentrations higher by an order of magnitude. The difference in concentrations may result from the time dividing both studies, both in the context of continuous bioaccumulation of these pollutants and the accuracy of measuring apparatus, which could prevent the detection of some OCPs and thus lowered the sum of the individual chemical compounds concentrations.

The OCPs concentrations in adipose tissue of other birds depend strictly on the species, likely in connection to their dietary preferences. The content of DDTs was lower in 1967 than in 2009, in the fat of not only penguins, but also other bird species (e.g. brown skua, blue-eyed shag, antarctic tern and snowy sheathbill) (Tatton and Ruzicka, 1967; Taniguchi et al., 2009). Furthermore, HCHs were several times more concentrated in other birds than penguins (Taniguchi et al., 2009). It was also found that brown skua fat had higher concentrations of HCB than penguin and other bird species fat, which may be due to the fact that brown skua is at a higher trophic level. Finally, significant concentrations of DDTs, HCHs, and drins, have been found in various sections of the penguin digestive tract. The concentration of these OCPs ranged from 1.49 to 2.67 ng/g in the case of droppings (Sun et al., 2006), while in stomach contents it was approximately 1 ng/g (Tatton and Ruzicka, 1967).

Schiavone et al. (2009) compared the content of selected OCPs in eggs of three penguin species and found the lowest DDTs and HCB values in gentoo penguin eggs which contained 3.7 ng/g HCB and 15 ng/g DDTs. Concentrations in chinstrap penguin eggs were slightly higher (3.8 ng/g HCB and 17 ng/g DDTs), while the Adélie penguin eggs exhibited the highest levels (7.63 ng/g HCB and 23 ng/g DDTs). Since these species live in the same area, the differences in chemical concentrations may be ascribed to factors such as diet, reproductive

status, ecological niches, and migration behaviour. Hence the eggs of different bird species can provide information on the degree of the species exposure to OCPs. For example, the HCB concentrations in the eggs of south polar skua and three species of penguins indicated a decrease with increasing trophic position (Mello et al., 2016). The levels of DDTs in south polar skua eggs were many times higher than in the case of penguin eggs, which indicate a high exposure of south polar skua to this pollutant class.

Pinnipeds are a common group of animals on the Antarctic coasts and islands. The OCPs content in their adipose tissue varies between the species, for example in connection to their dietary preferences. Southern elephant seal fat samples from Elephant Island were characterized by the highest concentrations of DDTs among other pinnipeds species (187.72 ng/g, lw) (Miranda-Filho et al., 2007). This value was similar to the content of these compounds in pinniped fat from King George Island (Cipro et al., 2012), which ranged from 14.4 to 168 ng/g lw, depending on the species. The highest concentrations of chlordanes and HCB were found in Weddell seal fat, which were 37.87–106.17 and 94.57–340.66 ng/g lw, respectively (Vergara et al., 2019). On the other hand, Crabeater seal blubber contained the most HCHs (75.70–111.15, ng/g lw) (Vergara et al., 2019). Both the latter pinniped species with the highest concentrations of the mentioned OCPs originated from the vicinity of Cape Shirreff Field Station (Livingstone Island). However, when Schiavone et al. (2009) also determined the concentrations of DDTs and HCB in the antarctic fur seal blubber living on Livingstone Island, they obtained values below the detection limit. On the other hand, the highest concentrations of endosulfans (21.15 ng/g, lw) and drins (82.4 ng/g, lw) occurred in the antarctic fur seals from King George Island (Schiavone et al., 2009).

The OCP concentrations in the liver of Southern elephant seal and Antarctic fur seal also differed: in favour of the Antarctic fur seal in the case of DDTs concentrations, and in favour of the Southern elephant seal for HCB (Cipro et al., 2013; Schiavone et al., 2009). The Southern elephant seal liver was also found to contain 1.41, 6.88, 2.72 and 37.7 ng/g lw of HCHs, drins, endosulfan and chlordanes, respectively (Cipro et al., 2013). The concentration of DDTs in Antarctic fur seal muscle (103 ng/g, ww) was similar to that in Southern elephant seal liver (98.7 ng/g, lw), and HCB concentration on those samples was lower than in the liver of both species (Cipro et al., 2013; Schiavone et al., 2009).

Significant concentrations of selected OCPs were also found in the aquatic organisms which for the most part constitute food for the animals described above. This shows that OCPs can be found at the lower levels of the food chain, too. Lana et al. (2014) determined the sums of OCPs in muscle, liver, gonads, and gills of fishes. The authors found the highest concentrations of DDTs in *Notothenia rossii* fish (253.6 ng/g, lw), and of HCHs in the *Notothenia coriiceps* fish species (61.02 ng/g, lw) (Lana et al., 2014). Furthermore, the concentrations of other OCPs in the aquatic organism tissues were also determined in other locations (Cipro et al., 2013; Strobel et al., 2018), and the highest concentrations of HCB (8.56 ng/g ww), drins (1.11 ng/g, ww) and chlordanes 3.94 (ng/g,ww) were found in the samples of Nacella concinna soft tissue. Finally, endosulfans peaked in Notothenia spp. muscle (Cipro et al., 2013).

4. Possible consequences of the presence of organochlorine pesticides for Antarctic fauna

Contemporary research (Mello et al., 2016; Strobel et al., 2018; Vergara et al., 2019) continues to show the presence of OCPs at various Antarctic trophic levels, despite the efforts to reduce their emissions. Climate conditions in Antarctica favour the persistence of OCPs. Several publications (Schiavone et al., 2009; Cipro et al., 2013; Lana et al., 2014) have highlighted the fact that Antarctic animals bioaccumulate and biomagnify these pollutants and can pass them on to their offspring. As mentioned previously, OCPs have a high affinity for fat, which acts as energy storage in the cold climate. This makes the southern polar food network especially sensitive to such contaminants. Fig. 4 shows a diagram of the OCPs circulation in the abiotic environment, which then impacts the aquatic and semi-aquatic living organisms.

Due to biomagnification, top predators are particularly vulnerable to OCP contamination (Schiavone et al., 2009). For example, seabirds whose main food is fish have higher OCP contents in their tissues compared to non-predatory species. A further factor deteriorating the birds resistance to xenobiotic compounds is their poor ability to metabolize those (Corsolini et al., 2007). Fig. 5 shows the most widespread animals on King George Island (South Shetland Islands, Marine Antarctica). The most common sea birds are penguins which are an important element of both marine and terrestrial ecosystem of the Antarctic. They mainly eat krill, but also include fish in their diet depending on the availability of food (Olmastroni et al., 2000). Adélie penguins eat up to 99% of krill. Penguins, like other birds of prey, are characterized by a higher content of OCPs and a lower level of detoxification of the body (Corsolini et al., 2007) than lower trophic level organisms, since birds cannot remove xenobiotics during gas exchange (breathing) and dermal diffusion. The removal of harmful substances can only happen through excretion and biotransformation (Goerke et al., 2004). Compared to krill, Weddell seal and southern elephant seal, which mainly feed on fish and cephalopods, show stronger biomagnification, by up to two orders of magnitude (Goerke et al., 2004).

Tanabe et al., 1997 showed that POPs are transported from mammals' fat to offspring along with their mother's milk, due to their good fat solubility. Since the milk of marine mammals is extremely high in lipids, juveniles are particularly vulnerable to POPs exposure. The Antarctic fur seal milk can be up to 39.8% fat (Goldsworthy and Crowley, 1999). Nakashima et al. (1997) found that in addition to breastfeeding, mammals are exposed to the penetration of POPs into their bodies through the uterus before birth. Other studies (Pastor et al., 1995; Drouillard and Norstrom, 2001) claim that the concentrations of contaminants including OCPs in the eggs of waterbirds correspond to those in maternal tissues. Considering these relationships, it is considered that if developing embryos are exposed to the same POPs concentration as mature individuals, and are more susceptible to chemical pollution, we will most likely observe toxic effects (Schiavone et al., 2009). Fig. 6A presents the biomagnification process on the example of the sum of DDTs in the tissues and eggs of Antarctic animals. In addition, Fig. 5B shows a food network occurring between the described Antarctic environment animals (Fig. 6A).

Fish can biotransform p, p'-DDT in to a stable metabolite, p,p'-DDE, and on this basis it can be determined when DDT has entered the aquatic environment (Vives et al., 2005). This means that the higher the p, p'-DDE/DDT ratio, the earlier the DDT had been emitted into the environment (Yogui et al., 2003). Based on this ratio, van den Brink et al. (2011) showed that p,p'-DDE concentration levels proportionally decrease in Antarctica pelagic organisms, while they increase in benthic organisms, which suggests a fresh input of contaminants into the pelagic biota, while the concentrations in benthic organisms approximate the total environmental burden of OCPs in Antarctica.

The HCH isomers are characterized by different properties which affect environmental stability and biodegradation of each of them (Phillips et al., 2005). For example, it was found that the α-HCH isomer bioaccumulates, while the β-HCH is stable to enzymatic degradation, making it more persistent in biota and more likely to biomagnify (Cipro et al., 2010; Tanabe et al., 1997). Based on the levels of HCH isomers in fish tissues, it was discovered that gonads are the main organ in which HCHs accumulate, which is a threat to the reproductive system (Lana et al., 2014). In addition, during the reproductive phase of catfishes and carps, these compounds are transported from the liver to the ovary, which results in reproductive disorders (Singh and Singh, 2008).

Based on POPs concentrations in the tissues of seabirds, it was concluded that the exposure to these chemicals in the Antarctic ecosystem

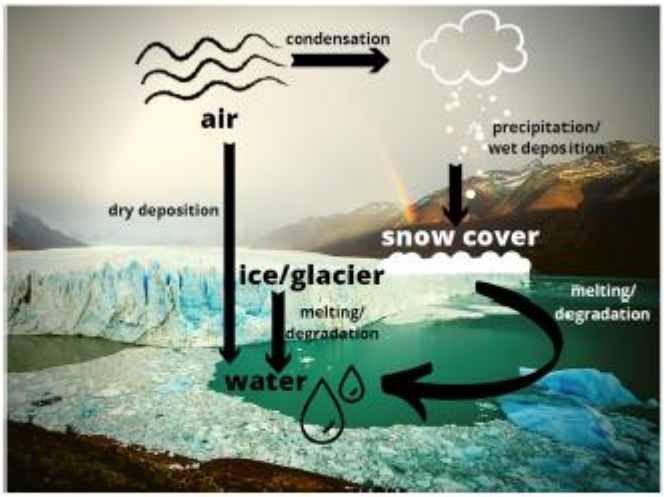

Fig. 4. Diagram of OCPs circulation in the Antarctic environment. The project was created based on publications collected in Tables 1 and 2.

decreased reproduction and survival rates, while it also increased the parasitic load (Sagerup et al., 2000; Bustnes et al., 2003, 2004). Other noted impacts were an increased asymmetry of the wings and the occurrence of immunohematological disorders. Moreover, it was found that organochlorine pollutant loads can determine the proliferation of leukocytes in glaucous gulls (Henriksen et al., 2000). Grasman and Fox, 2001 showed that significant concentrations of POPs may cripple the immune system cells functioning, consequently leading to an intensification in the production of these cells to compensate and fight back against low tier infections. The final effects of the described POPs-induced immunosuppression are infections, a disruption in the production of heterophile antibodies and lymphocytes (Grasman, 2002; Bustnes et al., 2004), and an increased exposure to parasitic diseases (Sagerup et al., 2000).

Fig. 5. Selected examples of the most common animal species on King George Island (South Shetland Islands, Marine Antarctica). Pictures were taken by J. Potapowicz during a scientific expedition to the Polish Antarctic Station in 2019.

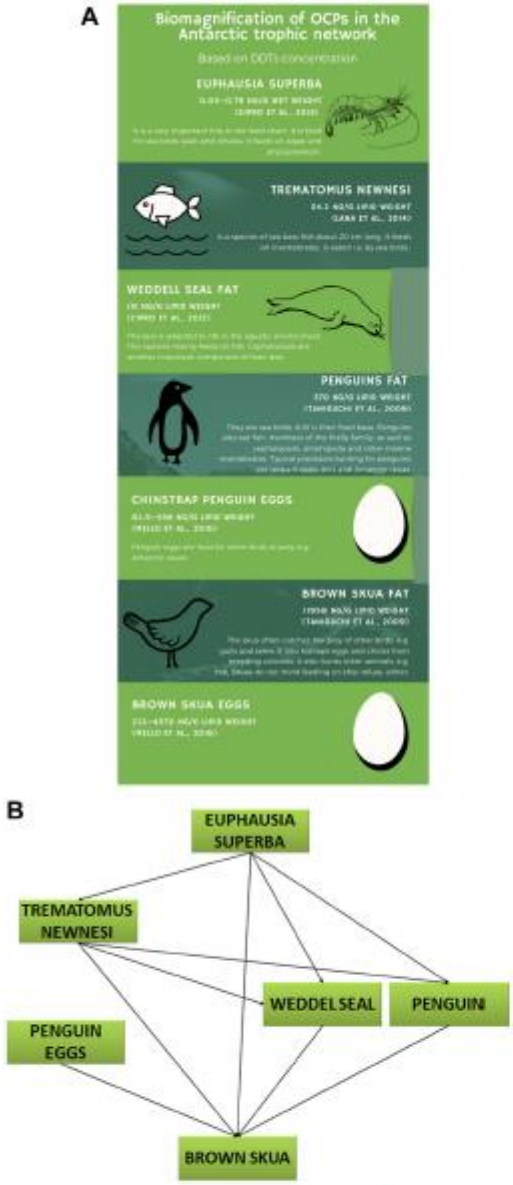

Fig. 6. A. Biomagnification process on the example of DDTs in tissues and eggs of Antarctic animals. B. An example of a food network occurring in the Antarctic environment in which biomagnification of OCPs is possible.

5. Conclusions

OCPs occur in Antarctic waters and biota and constitute a threat to the proper functioning of aquatic organisms. OCPs are characterized by a long residence time in the Antarctic environment, thus they persist even after a long period following emission. The reason for this is the properties of OCPs: slow degradation and the ability to accumulate in the Antarctic environment. As a result of climate change, there may also be secondary effects: accumulation of these chemicals in the Antarctic regions affected by temporary cooling and their reemission in the warming areas.

The most commonly detected OCPs in the Antarctic environment are DDTs, HCHs, HCB, aldrin, dieldrin, endrin, isodrin and chlordanes. The presence of OCPs was identified in various aquatic environments of the Antarctic (seawater and polynya water, freshwater, porewater, snow, firn and ice) and significant concentrations were found in biota. The presence of OCPs was confirmed in multiple tissues of aquatic organisms, bird eggs, and the content of the digestive tract of animals at higher trophic levels. Both OCPs and their degradation products negatively affect the living organisms in Antarctica, disrupting the natural ecosystem.

Due to the accumulation of OCPs in the abiotic and biotic environment in the Antarctic, it is necessary to monitor the concentration of this class of pollutants. The persisting knowledge gaps concern mapping the sources of these anthropogenic pollutants, including the secondary accumulations in the environment, and their transmission pathways between individual elements of the environment. Only such comprehensive recognition of the OCPs emissions into the Antarctic environment would allow to limit their impact, which depends on the long-term organisms exposure to these compounds. As a global problem, finding its solutions will depend also on how effective are the legal regulations on the use of OCPs worldwide.

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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In the Antarctic environments, current challenges include assessing the contribution of individual sources of pollution, among which we distinguish direct anthropogenic and natural global and local sources. In addition, emissions from melting glaciers (global scale) and snow, after deposition contaminants from the atmosphere (seasonal impact) are also important. Exploring this topic is particularly important given the ongoing climate change that is affecting sensitive polar environments. Moreover, the interest in the subject of chemical pollutants in Antarctica is significant because of their toxic effect on the functioning of sensitive living organisms in this area. As part of the research proposed, a comprehensive set of data on contaminants concentrations in various elements of the Antarctic environment was established. Physico-chemical in-situ measurements, chemical analyses and comprehensive data analysis of samples from various elements of the Antarctic environment enable a better understanding of the interactions and mechanisms between individual groups of chemical compounds in cold climate environments. Figure 2 shows the method by which the doctoral dissertation was conducted and how the sequence of individual studies was structured to verify the main hypothesis.

Figure 2. Structure of research goals leading to verification of main hypothesis

4.2 Characteristics of the case study region: Maritime Antarctica

Maritime Antarctica includes the South Sandwich Islands, the South Shetland Islands and the west coast of the Antarctic Peninsula, the adjacent archipelagos and surrounding waters. This area is characterised by the formation of a specific climatic zone [42]. As for the soils from this area, compared to other Antarctic climate zones they are distinguished by greater weathering and development [43,44]. The Maritime Antarctic climate, which is moist and much less extreme than on the continent, favours the processes of soil development [42]. The characteristic feature is the dominance of clay-sized material, which is related to chemical weathering, which is much more active here than elsewhere in Antarctica [45]. Due to the accumulation of guano (from seabirds, and especially penguins) in the Maritime Antarctic environment, there is a high availability of nutrients, especially phosphorus and nitrogen [46].

It is noteworthy that in humid climate conditions, substances washed out from guano decomposition react with the substrate, creating a wide phosphatised zone underneath [47]. The main soil formation process in Maritime Antarctica is phosphatisation, which is the cause of the formation of so-called ornithogenic soils [42,44]. Their occurrence is unique in the entire Antarctic and they are different from those of the continent [48]. Ornithogenic soils are composed of mineral and organic materials influenced by birds [49]. The structure of this type of soil has a high content of gravel that has been partially transported by birds, e.g. on the surface of feathers [50]. The soil formation processes of ornithogenic soils are of great importance in the coastal areas of Antarctica in the context of shaping this pristine environment [51,52].

The conditions in Maritime Antarctica favour the formation of deep and clayey soils [50]. Faecal and urinal organic deposition by marine birds influences many of the characteristic chemical, physical, mineralogical and micromorphological properties of ornithogenic soils [42,43]. Most clay-size particles are secondary phosphates and are distinguished by a relatively low pH value and, as well as nutrients, a high content of organic matter [49]. In old Antarctic ornithogenic sites, there are oases of plants composed mainly of mosses and lichens, where they have favourable conditions for

growth. In the case of active penguin rookeries, the conditions for plant growth are unfavourable due to toxic over-manuring and trampling by animals [53].

Intensive deglaciation is being caused by an increase in mean annual air temperature in the second half of 20th century in the Maritime Antarctic [54,55]. In this region, processes occurring in glaciers and snow packs are closely interrelated with terrestrial and marine ecosystems, such that the current state of ecosystems depends on the retreat of glaciers and melting snow cover [56]. In addition, the melting of snow and ice masses in which chemical pollutants have accumulated, together with the runoff from them, have an impact on the physical and biological processes of the catchment areas and coastal marine environments [56].

4.2.1 Western shore of Admiralty Bay (King George Island) and the sea belt as an area for evaluating human footprint

The sampling area (Fig. 3) is located by the western shore of Admiralty Bay on King George Island (South Shetland Islands, Maritime Antarctica). The region of South Shetland Archipelago is characterised by a moderate thermal range in combination with summer rains and high cloudiness. In addition, the climate in this area would be characterised as cold and maritime [54,57]. Unfortunately, in recent years, temperature changes have been observed in the research area, and these are part of global climate warming [58]. There has been an increase in temperature in the Antarctic Peninsula of ~0.5 °C/decade since 1950 [59], though a slight decrease has been recorded at the beginning of 21st century [60,61]. The King George Island has an area of about 1400 km^2, making it the largest island of the South Shetland Archipelago. Its area is less than 5% free of ice during the summer, but generally it is glaciated [62].

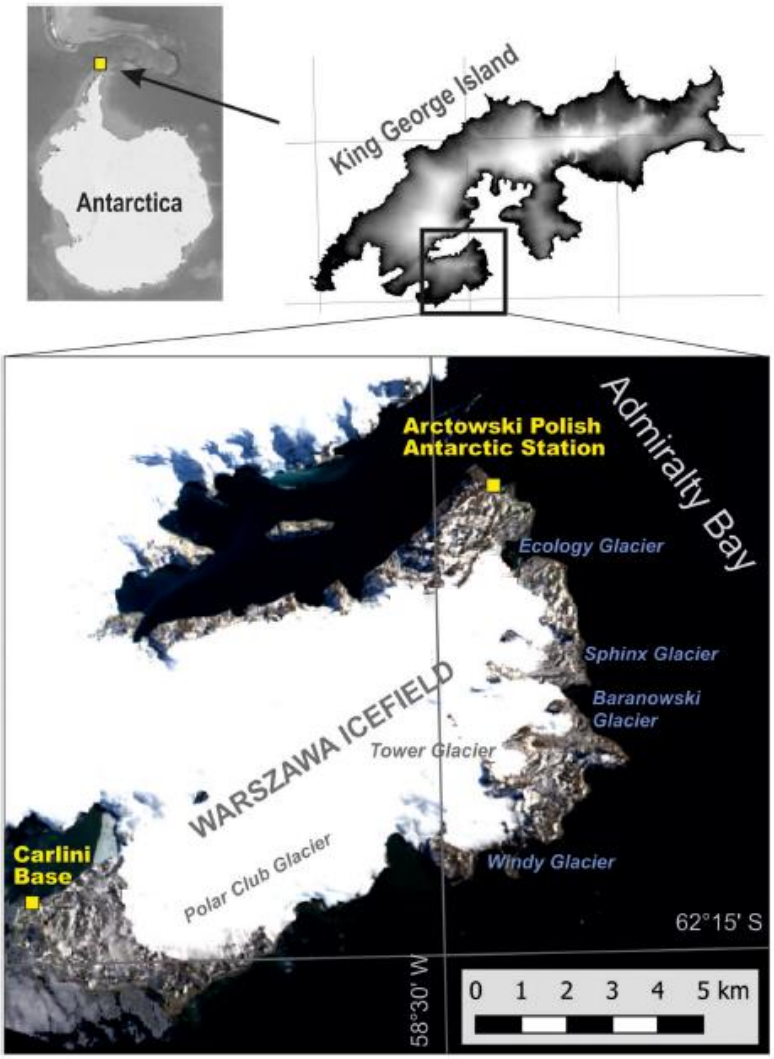

Figure 3. Location of the research area (based on Landsat Image LC08_L1GT_217103_20180309_20180320_01_T2 – Level 2, obtained from www.usgs.gov, Google Earth application) (Google Earth, 2018; USGS.gov, 2018, p. 08)

Rock formations occurring in this area are composed of relatively young Palaeocene-Oligocene-age rocks [63]. They are characterised by the presence of lavas and volcanoclastic rocks (debris flow deposits – breccias and tuffs, and laharian deposits) of basaltic and andesitic characteristics, interlayered with fluvial sediments [63,64]. The study area (the western shore of Admiralty Bay) includes Antarctic Specially Managed Area 1 (ASMA 1) and Antarctic Specially Protected Area 128 (ASPA 128), which were established mainly due to the presence there of a unique set of birds and marine mammals. ASMA 1 is a protected area of high environmental, historical and scientific values. In the areas covered by such protection, there is a risk of interference or an

increased impact on the environment. ASPA 128 is located south of the Henryk Arctowski Polish Antarctic Station (Fig. 4) and east of the Warszawa Icefield. To the south of the station there is a wetland area – a peatland called Jasnorzewski Gardens – which has numerous local depressions and is drained by a stream; further south there is Penguin Ridge, behind which there is the valley of Ornithologists Creek. Unlike the ASPA 128, ASMA 1 do not require a permit to enter.

Figure 4. Location of Henryk Arctowski Polish Antarctic Station on the western shore of Admiralty Bay. View from Jasnorzewski Gardens and Moss Creek (photo: Joanna Potapowicz)

The main creeks are fed both directly by atmospheric precipitation, snowmelt streams and a runoff from the melting Ecology, Sphinx and Baranowski glaciers. Most streams (e.g. Ornithologists, Siodło and Fosa Creeks) drain into the east of Admiralty Bay, forming mouths. Moss Creek ends its course by flowing into a lake that is separated from the bay by a narrow earth embankment. On the western coast of Admiralty Bay, based on the main geographical features, the following types of landscape can be distinguished:

1. new and relatively young paraglacial terrain in the forefields of glaciers;
2. areas previously uncovered by glaciers;
3. nunataks and their surroundings; and
4. beaches partially inhabited by Antarctic fauna.

Both the streams and the lakes that are the subject of research are located in catchments that differ in terms of the type of landscape and the main determinants of morphological and hydrological processes (Fig. 5). The catchments of Petrel Creek, Siodlo II and Fosa Creek are of the landscape types 1 and 3 above. However, the catchments of Petrified Forest Creek, Czech Creek, Vanishing Creek and Ornithologists Creek fit the second of the aforementioned landscape types (Fig. 6). Beach landscapes feature the mouth sections of all creeks, except Czech Creek and Vanishing Creek. As for Petrified Forest Creek, the beach has been changed by human impact resulting from the activity of the Arctowski station. An important factor associated with catchment processes in a research area is discontinuous permafrost, which occurs on King George Island at altitudes above 10–20 m a.s.l. (depending on location) [65,66] and is from 20 to 100 cm thick, and the active layer is from 50 to 180 cm deep. The specific nature of the catchment area in this area and the degradation of permafrost may affect the chemical composition of the water e.g. by increasing nutrient content [67]. Moreover, the areas recently uncovered by glaciers differ from the ice-free catchments in that they have a higher content of Fe and Al in water [20].

Figure 5. Catchments of creeks, glacier forefields and Admiralty Bay in the research area (photo: Joanna Potapowicz)

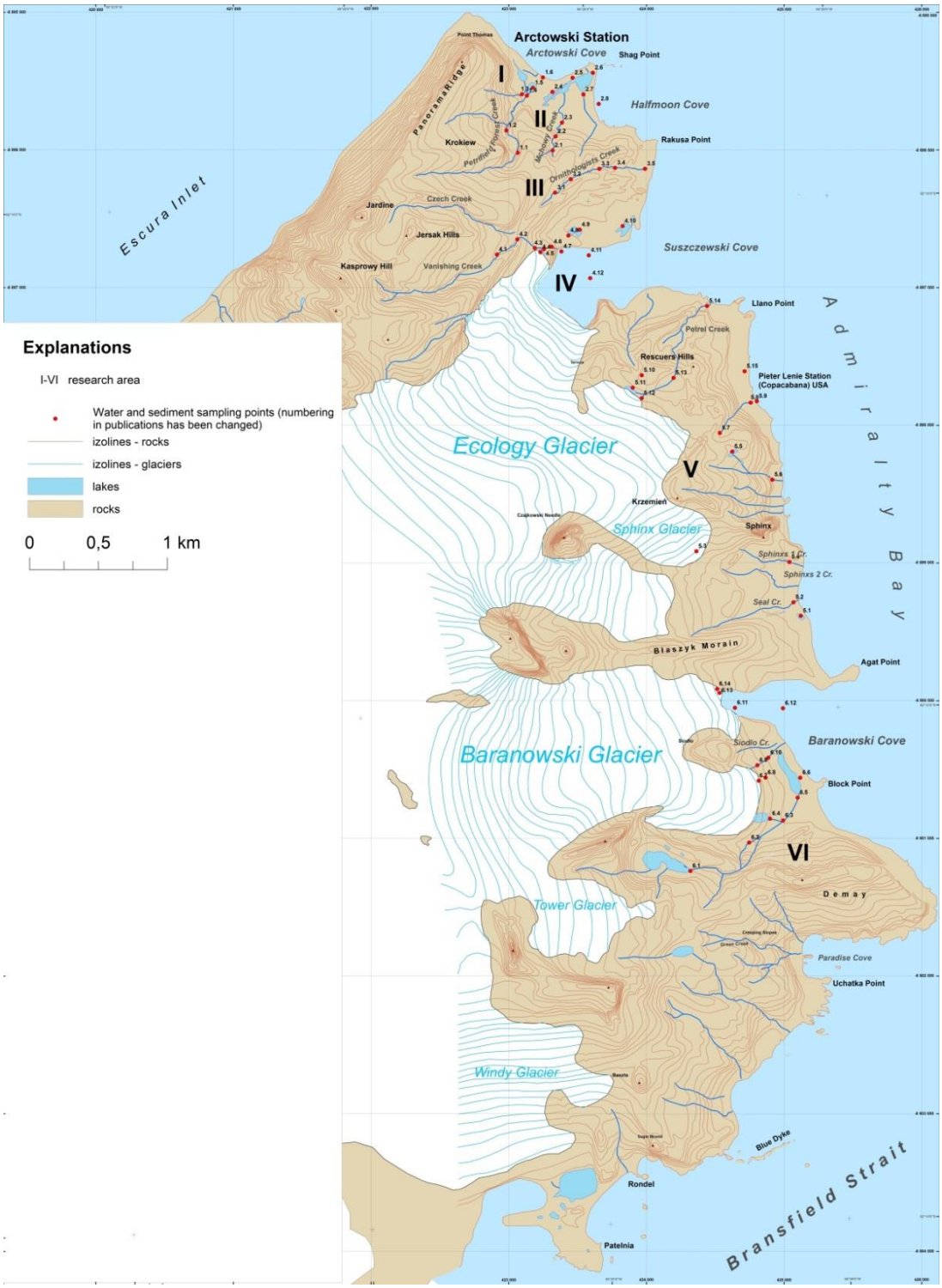

Figure 6. Location of watercourses, including those under study, on western shore of Admiralty Bay (prepared by Danuta Szumińska based on [68]; Landsat image LC82181032014016LGN00 obtained from www.usgs.gov; GoogleEarth application).

The vicinity of Admiralty Bay (62°02′S and 58°21′W) is a fjord-like area of 131 km^2 on the southern coast of King George Island [69]. The bay has many branches and can be divided into three main parts: Ezcurra Inlet to the south-west; Mackelar Inlet to the north; and Martel Inlet to the north-east [70]. Moreover, the central part of the bay connects these inlets to the open waters of the Bransfield Strait. On the coast of Admiralty Bay there are scientific stations operated by Poland (Henryk Arctowski), Brazil (Comandante Ferraz) and Peru (Machu Picchu) [71,72]. The liquid residues of septic tanks from the Polish Antarctic Station are discharged to Admiralty Bay. The wastewater discharge point is at Point Thomas (62°10′S and 58°30′W) on the south side of the entrance to Ezcurra Inlet. This location and the depth of the bay, which is more than 550 m deep at its deepest point [73], are expected to provide proper conditions for the "initial dilution" and "rapid dispersal" of discharged wastewater. For this reason, anthropogenic pollutants emitted by the discharge of sewage also became the subject of my in-depth research.

5. Aim of doctoral dissertation

The **main objective** of the research conducted as part of the doctoral dissertation was **an evaluation of the Antarctic environmental contamination state via an in-depth chemical analysis of various elements of the Antarctic environment**, taking into account whether and to what extent compounds classified as pollutants re-emitted from secondary sources such as snow cover or glaciers can significantly affect the concentration of these chemical compounds in freshwater, sea water, sediment and soil, and what the possible impacts are – whether seasonal (during summer thaws) or long. Additionally, endogenous anthropogenic sources of pollutants (untreated wastewater discharge) were evaluated, together with the possible influence on the marine environment.

Main hypothesis:

A holistic view and a wide range of chemical analyses, including of new and emerging pollutants, in the selected Antarctic environments may constitute the basis for better evaluation of the human contamination footprint in the study area.

Detailed hypotheses:

1. Physicochemical parameters of creeks and lakes depend on the water feed source [verification: **Publication III**].

2. Water–sediments–snow interactions influence pollution transport and distribution in the study area [verification: **Publications IV–VI**].

3. Untreated wastewater discharge into Admiralty Bay constitutes a threat to the marine Antarctic environment [verification: **Publications VII–VIII**].

Verification of the hypotheses presented above would enrich information on the long persistence of these chemicals in the Antarctic environment, as well as helping improve models of the spread of pollutants in polar areas and assessments of ecosystem damage. In addition, information could be obtained as to whether the main determinants of the chemical composition of water, snow and sediments are from local or global sources (e.g. LRAT). These extensive, valuable and hitherto unprecedented datasets on contaminants

in the Antarctic could be used to validate existing environmental fate models and identify threats to local fauna. Such a wide approach in this area has not been described in the scientific literature to date.

In addition, during the implementation of the doctoral dissertation, specific research goals were set, such as:

- qualitative and quantitative analysis of selected chemical compounds, including those classified as pollutants in water samples (fresh and marine), sediments and snow,
- analysis of the environmental fate of pollutants using chemometric tools and air-mass trajectory analysis,
- distinguishing the origins of chemical compounds present in the studied environmental samples from the western shore of Admiralty Bay,
- environmental assessment of selected organic pollutants which may affect the functioning of living organisms in Antarctica.

The implementation of specific research objectives made it possible to verify the hypotheses. The course of work is described in detail in Chapter 6.

6. The course of research work

The research carried out as part of the doctoral dissertation is interdisciplinary. To enrich the interpretation of the results of chemical analyses, specialists in the field of analytical chemistry, hydrology, geology, biology, microbiology and geography were invited to cooperate. Using the many years of experience of experts from this team, the tasks necessary to verify the hypotheses set out herein were planned.

The research began with the development of site locations, sampling concepts and procedures. The research area and its characteristics are described in detail in Chapter 4 "The genesis of research work". The measurement points were not constant during the verification of individual hypotheses, due to the variety of tested samples, as is described in the publications constituting the basis of the doctoral dissertation. Another task was to carry out work in the Antarctic terrain, which included sampling of surface waters, sediments, snow and wastewater, as well as their appropriate preparation for transport. Before determining selected chemical compounds in environmental samples, it was necessary to develop methodologies, and to select, optimise and validate analytical procedures. The results of physicochemical measurements and chemical analyses were compared against data obtained over the years 2016–18 and included, for example, meteorological, hydrological and geological data.

6.1 Summary and metrological characteristics of selected analytical techniques used for chemical analyses

During the implementation of the research plan, a multi-parameter database of physicochemical parameters and a wide range of compounds from various chemical groups was built up. The following is a summary (Table 1) including the modern analytical techniques used for the qualitative and quantitative analysis of many analytes during one measurement cycle.

A necessary part of applying any analytical method is its validation. This includes testing during the measurement of important features characterising the method, such as: limit of detection (LOD), limit of quantification (LOQ), repeatability, reproducibility, correctness, sensitivity, uncertainty, accuracy, linearity range, recovery, selectivity,

specificity, resistance to changing external conditions [74]. This subchapter presents the basic validation parameters of the methods used during the research (Table 2).

Table 1. Summary of specifications of measuring equipment used in the chemical research

ANALYTES/ PARAMETERS DETERMINED	MEASUREMENT APPARATUS/METHODS
CHEMICAL RESEARCH	
PHYSICOCHEMICAL PARAMETERS	
pH/temperature	pH-meter/thermometer: Elmetron CC-105 with GP-105 head
Conductivity	Conductivity method: Elmetron CC-105 conductometer
Redox parameter	HQ40d portable multimeter, IntelliCAL MTC 301
Chemical oxygen demand (COD)	Spectrophotometric methods: XION 500 Spectrophotometer (Dr Lange, GmbH, Germany)
IDENTIFICATION AND QUANTITATIVE ANALYSIS	
INORGANIC ANALYTES	
Cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+})	Ion chromatography (IC): DX ICS 3000 System, Dionex Corporation, USA mobile phase: 38 mM methanesulphonic acid; conductivity detector
Anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-})	Ion chromatography (IC): DX ICS 3000 System, Dionex Corporation, USA mobile phase: 4.5 mM CO_3^{2-}, 1.4 mM HCO_3^-; conductivity detector
Metals and non-metals (Bi, U, Cs, Pb, Ag, Ba, Cd, Co, Cu, Mo, Rb, Tl, Cr, Mn, Sr, Ni, Al, Li, Zn B, As)	Inductively coupled plasma mass spectrometer – ICP-MS Thermo X Series II with 3rd generation collision cell technology with kinetic energy discrimination (CCT KED), ICP-MS 2030 (Shimadzu, Japan)
Inorganic nitrogen compounds (N-NH_4^+, N-NO_3^-, and N-NO_2^-)**, total nitrogen** (TN)**, phosphate phosphorus** (P-PO_4^{3-}) **and total phosphorus** (TP)	Spectrophotometric methods (XION 500 spectrophotometer, Dr Lange, GmbH, Germany)
ORGANIC ANALYTES	
Total Organic Carbon (TOC)	Total Organic Carbon Analyser TOC-$V_{CSH/CSN}$, SHIMADZU (Method of catalytic combustion [oxidation] using nondispersive infrared sensor [NDIR])
Analysis of pharmaceuticals and personal care products (PPCPs) – 172 compounds (carbamazepine, diclofenac, imidacloprid, losartan, metoprolol, naproxen, oxazepame, trimetoprim, benzotriazole, ketoconazole, venlafaxine, zolpidem, bisphenol A, estrone, 3,4-Methylenedioxyamphetamine, acetaminophen, atorvastatin, caffeine, cetirizine, clindamycin, N,N-Diethyl-meta-toluamide, ketoprofen, lidocaine, loperamide, metformin, methyldopa, para-aminobenzoic acid, trimethoprim, benzophenone 1, caffeic acid, ibuprofen, nimesulide)*	Ultra-high performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS): Waters Acquity ultra-high-performance liquid chromatography UPLC H-Class with the Quaternary Solvent Manager (QSM) (Waters, Milford, MA). A Xevo TQ-S^{TM} triple quadrupole mass spectrometer (Waters Micromass, Manchester, UK) was equipped with a Z-spray electrospray interface. Ultra-high-performance liquid chromatography (UHPLC) – high-resolution mass spectrometry (HRMS) system with a Q Exactive Focus Orbitrap equipped with a heated electrospray ionisation source (H-ESI II) (Thermo Scientific, Bremen, Germany)
Polycyclic Aromatic Hydrocarbons (PAHs) – naphthalene, acenaphtylene, acenaphtene, fluorene, phenantrene, anthracene, fluoranthene, pirene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene	Gas chromatography tandem mass spectrometry (GC-MS/MS): GC – Agilent 7890B (Agilent Technologies, USA) equipped with a 7693A automatic sample feeder, and a 7000D GC/TQ triple quadrupole (Agilent Technologies, USA)
Formaldehyde	Ultraviolet–visible spectrophotometry (UV-Vis): Spectroquant Pharo 300 Merck, Germany
Different groups of surfactants: sum of non-ionic surfactants (SNI), sum of cationic surfactants (SC) and sum of anionic surfactants (SA)	Ultraviolet–visible spectrophotometry (UV-Vis): Spectroquant Pharo 300 Merck, Germany

* Among the analysed compounds, only those identified in the tested samples are listed

The biggest challenge when testing samples from Antarctic areas is to obtain results that accurately reflect the actual state of the environment, which is hampered by the low level of chemical species concentrations in samples from this area. That is why quality controlling the analyses was such an important part of implementing my research.

Steps were taken during the method validation stage and sample analysis to obtain results that as closely as possible reflected the actual state of the Antarctic environment:

- All reference standards and reagents were of high purity grade (>98%).
- Only deionised Milli-Q water was used during each stage of the analyses.
- Already at the stage of sampling in Antarctica, blank samples were prepared that were then transported to Poland in the same conditions as the environmental samples. Then they were prepared using the same analytical procedure and the same reagents. These measures eliminated the influence of transport and the emission of chemical compounds from the sampler and reagents used for the determination of the selected analytes.
- Laboratory glassware (vials, beakers, pipettes, etc.) were washed each time as per good laboratory practice [75] to avoid cross-contamination between samples.
- In the case of chromatographic methods, in each series of 10 measurements, a blank and standard (with known concentrations of analytes) samples were introduced to eliminate the probability of sample contamination and to verify the correctness of the chromatograph operation.

Table 2. Selected validation parameters of the analytical methods used while conducting research.

PARAMETER/ANALYTE	Limit of detection (LOD)	Limit of Quantification (LOQ)	Measurement range	Confidence interval (cuvette tests)	Confidence interval (other types)
PHYSICOCHEMICAL PARAMETERS					
pH	-	-	0–14	-	±0.02
Redox parameter	-	-	-1500–+1500 mV	-	±0.1 mV
Conductivity	-	-	0.01 µS/cm – 400 mS/cm	-	±0.5 %
Chemical oxygen demand (COD)	0.6 mg/L	2.0 mg/L	5.0–60 mg/L O_2	±0.75 mg/L	-
INORGANIC ANALYTES					
CATIONS AND ANIONS					
Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}	0.010 mg/L	0.030 mg/L	0.1–1 mg/L; 1–10 mg/L; 10–100 mg/L	–	0.6–1%
F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	0.010 mg/L	0.027 mg/L	0.1–1 mg/L; 1–10 mg/L; 10–100 mg/L	–	0.6–1%
METALS AND NON-METALS					
Bi, U, Cd	0.0020 µg/L	0.0060 µg/L	0.006–1 µg/L	–	0.5–1.5%
Cs, Pb, Be, Rb, Ag, Cs,Th	0.0030 µg/L	0.010 µg/L	0.01–1 µg/L	–	0.5–1.5%
Tl	0.010 µg/L	0.030 µg/L	0.03–10 µg/L	–	0.5–1.5%
Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Ba, Sr	0.030 µg/L	0.10 µg/L	0.10–10 µg/L; 10–1000 µg/L	–	0.5–1.5%
P	0.060 µg/L	0.18 µg/L	1–100 µg/L	–	0.5–1.5%
Fe	0.30 µg/L	0.60 µg/L	0.60–10 µg/L; 10–1000 µg/L	–	0.5–1.5%
B	2.0 µg/L	6.0 µg/L	6.0–100 µg/L	–	0.5–1.5%

PARAMETER/ANALYTE	Limit of detection (LOD)	Limit of Quantification (LOQ)	Measurement range	Confidence interval (cuvette tests)	Confidence interval (other types)
NITROGEN AND PHOSPHORUS FORMS					
$P\text{-}PO_4^{3-}$	0.007 mg/L	0.020 mg/L	0.05–1.5 mg/L	± 0.010 mg/L	–
TP	0.007 mg/L	0.020 mg/L	0.15–4.5 mg/L	± 0.010 mg/L	–
$N\text{-}NH_4^+$	0.005 mg/L	0.015 mg/L	0.015–2.0 mg/L	±0.012 mg/L	–
$N\text{-}NO_3^-$	0.210 mg/L	0.629 mg/L	0.23–13.5 mg/L	±0.45 mg/L	–
$N\text{-}NO_2^-$	0.012 mg/L	0.037 mg/L	0.015–0.6 mg/L	±0.035 mg/L	–
TN	0.116 mg/L	0.350 mg/L	1–16 mg/L	±0.229 mg/L	–
ORGANIC ANALYTES/PARAMETERS					
TOTAL ORGANIC CARBON					
Total organic carbon (TOC)	0.030 mg/L	0.10 mg/L	0.15–10 mg/L	–	0.1–1.5%
PHARMACEUTICALS AND PERSONAL CARE PRODUCTS					
Analysis of pharmaceuticals and personal care products (PPCPs) – 172 compounds	0.030 ng/L	0.10 ng/L	0.10–50 ng/L	–	0.1–1.5%
POLYCYCLIC AROMATIC HYDROCARBONS					
Polycyclic Aromatic Hydrocarbons (PAHs)	0.030 ng/L	0.09 ng/L	0.09–50 ng/L; 10–1000 ng/L	–	0.5–5%
FORMALDEHYDE					
Formaldehyde (HCHO)	0.040 mg/L	0.10 mg/L	0.10–8.00 mg/L	±0.087 mg/L	
DIFFERENT GROUPS OF SURFACTANTS					
Sum of cationic surfactants (SC)	0.027 mg/L	0.05 mg/L	0.05–1.50 mg/L	±0.017 mg/L	
Sum of anionic surfactants (SA)	0.030 mg/L	0.05 mg/L	0.05–2.00 mg/L	±0.10 mg/L	
Sum of non-ionic surfactants (SNI)	0.062 mg/L	0.15 mg/L	0.1–7.5 mg/L	±0.075 mg/L	

Table 2 shows an overview of the validation parameters combining the groups of analytes. Only the lowest values of LOD are listed in the table; LOD and LOQ values for individual analysis cycles are available in the publications constituting the basis of this dissertation.

6.2 Characteristics of interdisciplinary tools used to interpret obtained data

Publications presented in the doctoral dissertation contain a detailed analysis of a multi-parameter database that allowed for an in-depth and interdisciplinary look at the environmental fate of the studied chemical species and the processes taking place in the Antarctic environment. Interpretation of the results of analyses of samples of surface waters, sediments, snow and wastewater was possible with the use of chemometric, geological or hydrological tools, among others (Table 3), which was necessary to verify the research hypotheses.

Table 3. Description of tools for interpreting chemical composition of tested environmental samples

PURPOSE OF USE	TOOLS	EFFECT
Identify main determinants of chemical composition of environmental samples	Principal Component Analysis (PCA)	On the basis of data reduction and/or structure detection in relationships between variables, it was possible to select the main determinants of the chemistry of the water, sediments and snow and interactions between individual chemical entities in the tested samples.
Estimation of the impact of permafrost degradation and glacial recession on chemical changes in environmental samples	Analysis of climate and weather conditions	Analysis of, inter alia, average daily air temperatures, sums of precipitation and wind directions provided a multidimensional view of the impact of climatic conditions on cryosphere changes.
	Geological and hydrological analysis of the research area	Because not all chemical entities present in environmental samples are anthropogenic, geological analysis was necessary to verify the natural sources of elements and chemical compounds present in water, snow and sediments. Additionally, hydrological analysis was used to characterise the chemical composition of the study areas by analysing the nature of the catchment.
	Analysis of the degradation and boundaries of permafrost and glacier fronts	The available literature data and detailed maps of the areas were used to present the extent of occurrence of glacier heads over the years. Satellite images were also used to determine the current range of glaciers. This analysis enriched the results of chemical analyses with a discussion on the impact of glacier recession on the chemistry of Antarctic samples.
	Analysis of Pearson correlation factors	Because some elements may be adsorbed to organic matter particles, analysis of correlation coefficients of TOC and selected elements and of correlations between elements will allow verification of their source.
Identification of sources of chemical compounds classified as pollutants	Air mass trajectory analysis	Performed according to the NOAA HySPLIT model based on Global Data Assimilation System meteorological data, this analysis assessed sources of pollution and directions of its spread on a global scale, with particular emphasis on the Antarctic region.

PURPOSE OF USE	TOOLS	EFFECT
Identification of sources of chemical compounds classified as pollutants	Concentration analysis of non-sea salt (nss) SO_4^{2-}	This was used to demonstrate the proportion of sulphate (VI) concentration not derived from sea salt.
	Volcanic activity analysis	This was used to interpret the determinations of PAHs that may come from a natural source, i.e. volcanic incidents. For a full picture, detailed analysis of contemporary and past volcanic phenomena was necessary.
	Analysis of diagnostic coefficients and percentage share of individual organic compounds, e.g. PAHs	Selected diagnostic factors were used to distinguish sources of compounds (e.g. PAHs) between petrogenic sources (e.g. oil spills) and pyrogenic sources (e.g. biomass combustion).
	Analysis of the percentage of compounds from particular groups of chemical species	The analysis of the percentage profiles of compounds, e.g. PAHs, PCPPs, ECs or individual cations and anions in tested samples enriched the information on the sources of origin of these chemical species.
	Analysis of no observed effect concentrations (NOECs) and risk quotients (RQs)	The analysis was used to compare NOEC values against selected Antarctic bioindicators. Moreover, RQs were applied to assess the potential aquatic ecological risks of detected and measured concentrations of PPCPs and ECs. This was necessary to achieve the research goal of assessing the risk that the studied chemical species pose to Antarctic ecosystems.

7. Description of results and discussion in terms of verification of research hypotheses

To verify the hypotheses put forward in Chapter 5 "Aim of doctoral dissertation", the western shore of Admiralty Bay (near the Polish Antarctic Station) was selected because, in this area, there has been relatively little research on the chemistry of surface waters, sediments and snow, e.g. [3,20,76,77]. In addition, it was decided to comprehensively analyse various types of environmental samples and mark a wide range of pollutants, which is a novel approach to understanding the fate of environmental chemicals and their interactions in this pristine area. During the research work, apart from the direct impact of pollutant emissions, the effects of the phenomena of permafrost degradation and glacier recession were also observed and were confirmed by changes in chemical characteristics in selected areas. All the hypotheses were verified on the basis of environmental samples taken from the west coast of Admiralty Bay.

7.1 Verification of detailed hypothesis 1: Physicochemical parameters of creeks and lakes depend on water feed source

The structure of the drainage network and the supply of watercourses in the periglacial Antarctic environment strictly depend on the intensive morphological processes [78,79] related to climate changes that have taken place in recent decades [54,80]. These changes resulted in the development of new ice-free areas with an initial drainage network characterised by highly dynamic hydrological processes [81]. The chemistry of water in Antarctica has been the subject of several publications. They concerned concentration ranges in water samples, but did not focus on the relationship between the chemical status and the characteristics of the Antarctic catchment area, due to the lack of comprehensive information on, for example, soil structure, conditions and geochemistry in this area [76,82]. Research to date indicates that the chemical status of surface waters in this area is shaped by natural factors, e.g geological structure, marine aerosols [76,83], and anthropogenic factors such as the infrastructure of research stations, tourism [20].

The verification of the first detailed hypothesis is presented in the journal *Ecological Chemistry and Engineering S*: **Potapowicz J., Szumińska D, Szopińska M., Czapiewski S., Polkowska Ż, , Electrical conductivity and pH in surface water as**

tool for identification of chemical diversity, *Ecol. Chem. Eng., S*, 27 (2020) 95-111 [publication III]. The article presents the influence of various sources of water supply on the physicochemical characteristics of the studied area, based on the parameters of temperature, pH and specific electrolytic conductivity (SEC_{25}). All measurements were conducted during a field campaign in January-February 2017 and were made in situ.

The results of surface water analyses on the western coast of Admiralty Bay show high variability of temperature (T) and specific electrical conductivity (SEC_{25}) along the watercourses, suggesting that some sections of the watercourses were more strongly fed by melting water from various sources of buried ice (including permafrost). Analysis of the obtained data confirmed that the waters fed with glacial ablation had SEC_{25} to 100 $\mu S \cdot cm^{-1}$, while the waters in the catchments without glacial supply, which were already under the influence of periglacial conditions, had SEC_{25} in the range of 100–250 $\mu S \cdot cm^{-1}$. In addition, statistical analysis showed that samples taken from areas in the early deglaciated catchments (Petrified Forest Creek, Czech Creek, Ornithologists Creek) are characterised by a higher pH/SEC_{25} ratio compared to water samples taken from the forefield of the glacier. The obtained results indicate the significant impact of soil background (geochemical factor) and glacier retreat on the formation of surface water chemistry on the western coast of Admiralty Bay. After analysing the results of the research, the hypothesis was confirmed. Moreover, described differences in the values of physicochemical parameters were the basis for undertaking more extensive research on the presence and environmental fate of pollutants on the western coast of Admiralty Bay in the following years.

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ELECTRICAL CONDUCTIVITY AND pH IN SURFACE WATER AS TOOL FOR IDENTIFICATION OF CHEMICAL DIVERSITY

Abstract: In the present study, the creeks and lakes located at the western shore of Admiralty Bay were analysed. The impact of various sources of water supply was considered, based on the parameters of temperature, pH and specific electrolytic conductivity (SEC_{25}). All measurements were conducted during a field campaign in January-February 2017. A multivariate dataset was also created and a biplot of SEC_{25} and pH of the investigated waters was performed. The average temperatures of the investigated waters were 0.10-8.10 °C. The pH values indicate that most of the water environments of the analysed area are slightly acidic to alkaline (5.26-8.50) with two exceptions: Siodło II Creek (9.26) and Petrified Forest Creek (8.95), which are characterised by greater alkalinity. At the measurement points closest to the Baranowski Glacier and Ecology Glacier, SEC_{25} values were the lowest (26.8-61.1 $\mu S \cdot cm^{-1}$), while the remaining values ranged from 79.0 to 382 $\mu S \cdot cm^{-1}$ for the whole studied area. Based on the results it is concluded that the periodic intensive inflow of ablation waters, combined with morphological changes in the glacier front, causes a significant variability in the outflow network, creating the conditions for changes in basic physicochemical parameters. Moreover, it is observed that local depressions in the terrain form sedimentation traps in which, alongside fine-grained deposits, compounds can accumulate that originate from *in situ* sedimentation and that are also associated with surface runoff from the melting of snow cover, buried ice and permafrost.

Keywords: surface water, electrical conductivity, pH, Admiralty Bay, Maritime Antarctica

Introduction

Drainage network formation and the feeding of creeks in paraglacial and periglacial environments of the Antarctic Peninsula depends on intensive morphological processes [1-4] related to climate changes that have been observed in recent decades [5-10]. Rapid glacier retreat observed over recent decades [4, 11-14] have resulted in the development a new ice-free areas with an initial drainage network characterised by highly dynamic hydrological processes [9, 15].

Water chemistry in the Antarctic has been the subject of several publications, e.g. [16-25]. However, the relation between chemical status and catchment features in Antarctic catchments is one of the less well-known, because of the lack of comprehensive

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information about, for example, soil patterns, permafrost occurrence, groundwater conditions and geochemistry. The collecting of this kind of data is typical in hydrological and hydrochemical analysis of catchments located in areas more easily accessible to field work, aerial photography, laser scanning, etc. Furthermore, the rapid glacier retreat that has been observed in recent decades in this area, e.g. [5, 6, 8, 10, 26], is causing rapid changes in the water network and has led to the observation of two main types of catchments: young paraglacial catchments, with creeks being fed by glacier thawing, and previously formed catchments without glacier-melt water supply.

Research to date indicates that the chemical status of surface waters in this area is shaped by both natural factors such as geological structure, marine aerosols, etc. [20-22, 24, 25] as well as anthropogenic factors. The infrastructure of research stations may have a negative impact on the environment in the form of pollutant emissions and is not without impact on the sensitive ecosystems occurring there [17, 24, 25]. In addition, the development of tourism has also been seen in recent years [24, 25], which is associated with an increase in pollutant emissions due to the higher frequency of passing ships. Therefore, one should agree with Kroto et al. [27], that the need to share and promotion the results of research related to environment arises. It is important especially in terms to sensitive polar ecosystems. Antarctica is also influenced by global anthropogenic activities, mainly due to the transport of pollutants over long distances by atmospheric (long range atmospheric transport, LRAT) [25]. The main aim of this study is to analyse the relation between electrical conductivity (SEC_{25}) and pH of water in creeks in both types of catchments. The detailed chemical status of some of the creeks has been provided before on the basis of samples collected in 2016 [25], but the limited number of sampling points along the creeks caused some difficulties with interpretation of factors related to diversification of the catchment. Moreover, taking into account a limited numbers of samples subjected to chemical analyses in Poland (limited on account of transportation limits and high analysis costs) it is important to find the general rules of chemical inorganic diversity based on simple measurements performed *in situ* in the field.

Hence, this paper aims to interpret SEC_{25} and pH data based on creeks and lakes in the western shore of Admiralty Bay in relation to the location of sampling sites (Fig. 1). This approach allowed us to analyse creeks with regard to the impact of the various water supply sources to determine the factors that alter water composition: e.g. soil background (geochemical factor), marine aerosols, glacier retreat, meteorological conditions, human activity and transport of nutrients by biovectors, e.g. penguins.

Study area

The research area is located on King George Island (the western shore of Admiralty Bay, South Shetland Islands, Antarctic Peninsula), 90 % of whose surface (1,310 km^2) is permanently glaciated [11] (Fig. 1). Deglaciation [14, 28] and related changes in the water network plays an important role in hydrological processes and is one of the factors that determines the chemical status of water bodies in the study area [25]. Changes in the distribution of glaciers at the western shore of Admiralty Bay between 1979 and 2014 are presented in Figure 1.

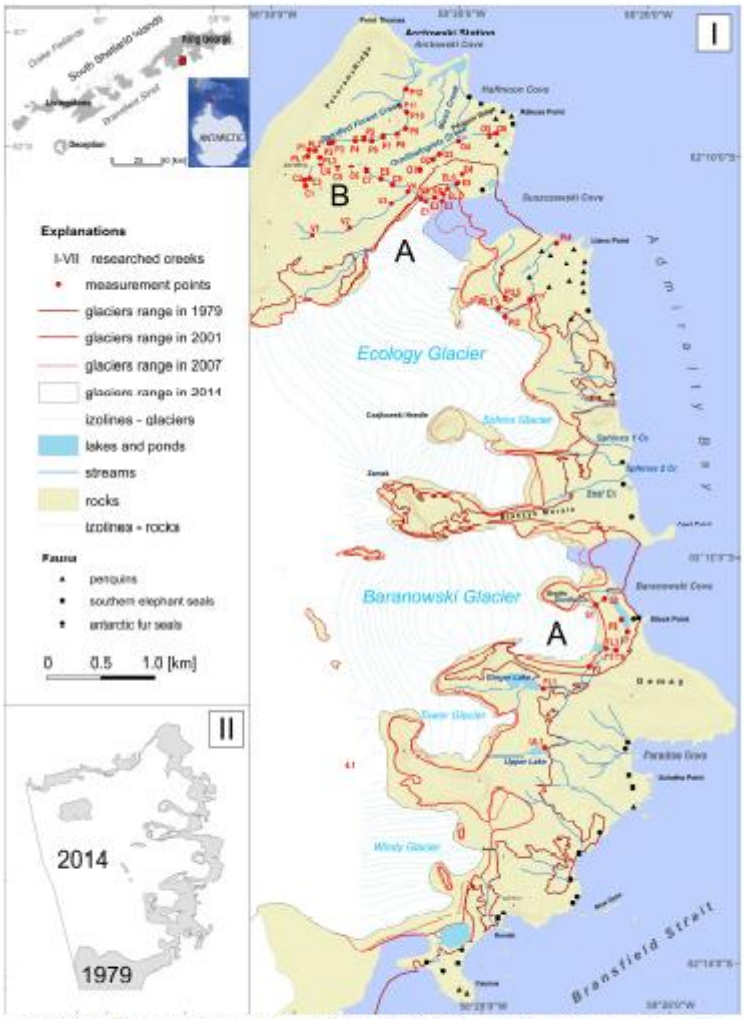

Fig. 1. Map of the western shore of Admiralty Bay (Maritime Antarctica) showing the location of the measuring points (I) and glaciers' retreat between 1979 and 2014 (II): A - creeks draining the area uncovered by glacier after 1979, B - creeks draining the area uncovered by glacier before 1979; P - measured points on creeks, PL - measured points on lakes (prepared based on [29]; Landsat image LC82181032014016LGN00 obtained from www.usgs.gov; GoogleEarth application)

The most significant changes have been observed in the parts of the glacier forefield that ranged close to the seashore in 1979 (Fig. 1). Petlicki et al. [14] calculated the mean vertical changes in Ecology Glacier from 1979 to 2016 at –57.9 ±10.1 m for the entire period, and –1.6 ±0.3 m per year. The authors' own calculation for the area presented in Figure 1 shows that the glacier horizontal retreat exceeded 700 m in some sections of the Ecology Glacier, 600 m in parts of the Baranowski Glacier, and 1,500 m at the border of the Tower and Windy glaciers. The total area of newly-formed ice-free terrain amounted to 8.67 km^2. This area has been subject to intensive morphological processes [30] and many new riverbeds have been established [15].

The intensive deglaciation is caused by an increase in mean annual air temperature during the second half of 20th century in the Maritime Antarctic, e.g. [5, 6, 9, 10]. Temperature changes observed in research area are part of global climate warming e.g. [26, 31]. According to Turner et al. [32] the temperature increase in Antarctic Peninsula of ~0.5 °C/decade since 1950, however slight decrease has been recorded at the beginning of 21st century [33, 34].

In 2017 the mean annual air temperature in the Bellingshausen station on King George Island was –1.8 °C, which is higher than the mean for the years 1968-2017 (–2.3 °C) (calculation based on data provided at www.rp5.ru). Total annual precipitation in 2017 was 727 mm, which was higher than the long-term mean of 697 mm. Measurements of SEC_{25}, pH and T were carried out between January 7th and February 7th 2017. At the time of measuring of pH, SEC_{25} and T in water (Jan 7 to Feb 7), average daily temperatures ranged between 1 and 6 °C (Fig. 2). The maximum daily temperature (10.1 °C) was noted on February 8th, and the minimum (0.1 °C) on January 16th. Snow cover occurred at the beginning of January and it rained on several days in both months. Total daily precipitation did not exceed 5-10 mm (Fig. 2). In addition to changes in air temperature, the accompanying processes have been also observed Maritime Antarctica, inter alia permafrost degradation [35], which indicates the impact of climate change on polar heat exchange systems.

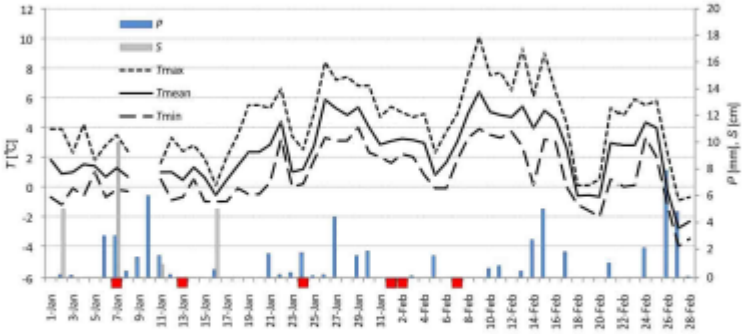

Fig. 2. Weather conditions Jan 1 to Feb 28, 2017 based on data from the meteorological station in the vicinity of the Arctowski Polish Polar Station. Abbreviations: P - precipitation, S - snow depth, T - temperature, days of measurements are marked in red

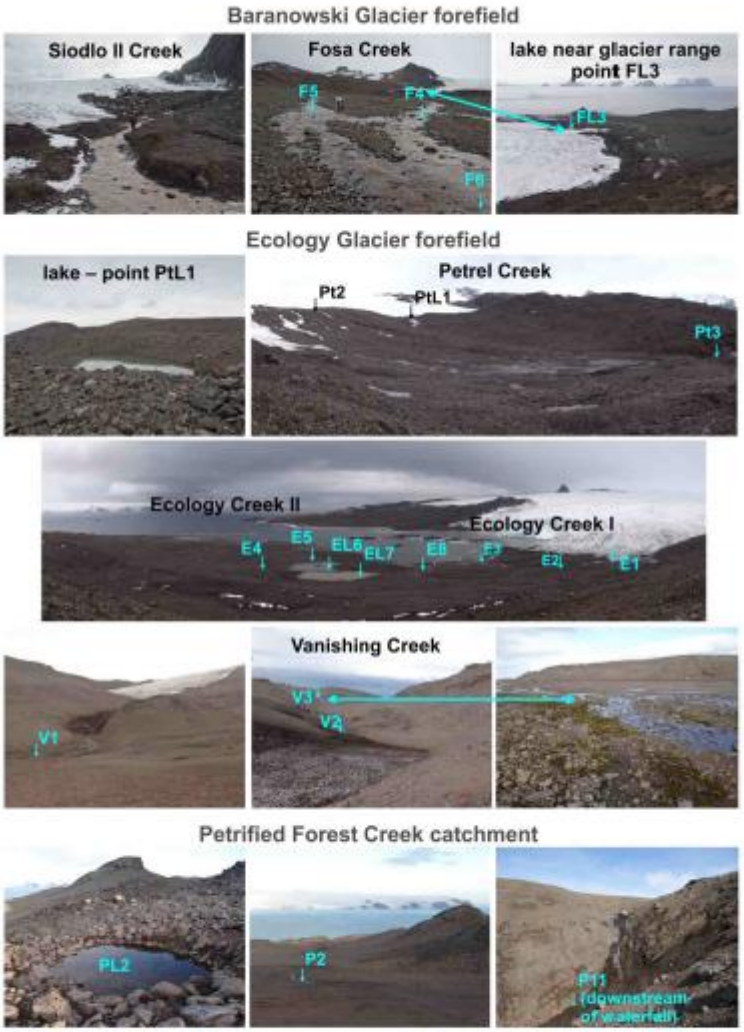

Fig. 3. Studied creeks and lakes at the western shore of Admiralty Bay (Feb-Jan 2017)

Taking into account the main geographical features of the research area, several main types of landscape can be distinguished:

1) new and relatively young paraglacial terrain in the forefields of glaciers;
2) areas previously uncovered by glaciers;
3) nunataks and their surroundings; and
4) beaches partially inhabited by Antarctic fauna.

The researched creeks (and lakes located in the watersheds) differ in terms of landscape (Fig. 3) and main factors determining morphological and hydrological processes. The catchments of Petrel Creek, Siodlo II and Fosa Creek are of the first and third landscape types. However, the catchments of Petrified Forest Creek, Czech Creek, Vanishing Creek and Ornithologists Creek are the second of the aforementioned landscape types. The mouth sections of all creeks, except Czech Creek and Vanishing Creek, are located in beach landscapes. In the case of Petrified Forest Creek, the beach has been changed by the human impact of the Arctowski station.

In terms of their geological structure, watersheds of Petrified Forest Creek, Czech Creek, Vanishing Creek and Ornithologists Creek are located within the Arctowski Cove Formation and the Point Thomas Formation, terrestrial volcanic and sedimentary groups [36]. In these units, basalt, and basaltic and andesite lava are interlayered with breccias and pyroclastics with andesite conglomerate lag intercalations. The watersheds of Ecology Creek and Petrel Creek are located in the forefield of Ecology Glacier, whereas the watershed of Fosa Creek is in the forefield of the Baranowski Glacier (Fig. 1). The highest sections of these watersheds are connected with the Llano Point formations and feature basaltic andesite lavas, alternating with scoria and breccias [36]. However, the forefield of the Baranowski Glacier also includes the Demay Point Formation consisting mainly of acidic volcanic rocks with andesite agglomerate and petrified wood fragments. Therefore, most of these particular areas consist of ground and marginal moraines - features of considerable hydration and low compaction.

An additional factor related to watershed processes is the discontinuous permafrost that occurred on King George Island at altitudes above 10-20 m a.s.l. [9, 30] with thicknesses ranging from 20 to 100 cm and active layer depth ranging from 50 to 180 cm. Additionally, the lower courses of Ornithologists Creek are inhabited by a few species of flora. This may change the chemical composition of the water, mainly by increasing nutrient contents [37]: *inter alia* PO_4^{3-}, NO_3^-, NH_4^+, and some microelements (e.g. Zn, Cu, Sr) [25]. Moreover, the areas recently uncovered by glaciers differ from the ice-free catchments in that they have a higher content of Fe and Al in water [25].

Methods

Research was conducted on nine creeks draining the ice-free area at the western shore of Admiralty Bay, between the Baranowski Glacier and the Arctowski Oasis, and on six lakes in the researched catchments (Fig. 1). Three streams drain the immediate forefield of the Baranowski Glacier (Petrel Creek - 0.33 km, Siodlo II Creek - 0.33 km and Fosa Creek - 1.1 km, downstream of Ginger Lake), and two drain Ecology Glacier (two short creeks of 0.2 km length, referred to in this work as Ecology Creek). In contrast to the other streams, the upper course of Fosa Creek is separate from direct glacier-melt water (Fig. 1). The other four studied streams (Vanishing Creek - 1.24 km, Czech Creek - 1.08 km, Ornithologists Creek - 0.92 km and Petrified Forest Creek - 1.62 km) are south-west and south of Henryk

Arctowski Research Station (Fig. 1). In all watercourses, measurements of SEC_{25}, pH and T were taken during a field campaign in January-February 2017 using a CC-105 conductivity meter and a CP-105 pH-meter manufactured by ELMETRON. The resolution of the Elmetron device was ±0.02 for pH; ±0.1 mV for conductivity and ±0.8 °C for temperature. The person measuring the field had lates gloves on. Particular attention was paid to ensure that the heads of the pH meter and conductivity meter are completely submerged under water. Measurements were taken on the surface water about 50 cm from the creek shore. The points where the water had laminar flow were selected as the measurement site.

Measurements sites were determined taking into account catchments' diversification and their possibility of supply by glacier-melt water. The was a total of 59 measured points (Petrified Forest Creek - 15; Czech Creek - 9, Vanishing Creek - 5, Ornithologists Creek - 6; Ecology Creek - 8; Petrel Creek - 5; Siodlo II Creek - 2; and Fosa Creek with the Upper Lake - 9). In the cases of Fosa Creek and Siodlo II Creek, measurements were taken three times (7 Jan, 10 Jan, 24 Jan), according to the progress of snowing and glacier ablation. In the other watercourses and lakes, measurements were conducted once between 1st and 7th February. There were 80 measurements in total (including repeat measurements in selected creeks).

Results

The statistical characteristics of the temperature, pH and conductivity values could be found in Table 1 for the entire data set, and in Table 2 for particular catchments. The temperature of water ranged between 0.1 and 8.1°C. The lowest temperatures were observed in creeks fed by melt water, namely Ecology and Siodlo II (Table 2). The pH of the waters ranged from 5.26 to 9.26. The skewness and kurtosis values indicate that temperature and conductivity were normally distributed in the data set, but pH has a strongly leptokurtic data distribution.

Table 1

Basic characteristics calculated based on entire datasets of measurement points

	Mean	Median	Min.	Max	St. dev.	Skewness	Kurtosis
T [°C]	3.65	3.70	0.10	8.10	2.11	0.082	−1.002
SEC_{25} [µS·cm^{-1}]	127	104	26.8	382	75.0	1.132	1.228
pH [-]	7.81	7.84	5.26	9.26	0.62	−1.118	5.323

T - temperature, SEC_{25} - conductivity

In terms of the distribution of measured parameters in individual catchments (Table 2), among the type-A streams (with the possibility of being fed by glacial melt water) Siodlo II Creek distinguishes itself for its low water temperature (Fig. 4A). In that creek, when the measurements were taken, all the water actually came from glacier ablation (Fig. 1, Fig 3). Similarly low water temperatures were measured at point FL3 in Fosa Creek (Fig. 4A) on all measurement dates, and in profile F4 on 10 and 24 January. Point FL3 is water of the lake at the front of Baranowski Glacier, while point F4 is located on its outflow stream (Fig. 1, Fig. 3). Point F5 is located in the profile at the end of the upper course of Fosa Creek, below point F2. Next, point F6 is after the confluence of Fosa Creek (F5) and its tributary from the lake (F4). The temperature distribution at these points indicated a strong inflow of glacier melt waters on January 10 and 24, which was the result of rising air temperatures in January (Fig. 2) and the associated intensive ablation. Regarding

watercourses without ablation water supply (Table 2, Fig. 4B), among the four analysed watercourses, Petrified Forest Creek is distinguished by its low water temperature, while the low water temperatures are created in the middle of its course (points P3-P5 and P9) (Fig. 1, Fig. 4).

Table 2

Basic characteristics of selected creeks (including lakes located in a particular catchment): A - catchments with glacier-melt supply of creeks, B - catchment without glacier-melt supply of creeks

Research area	Mean	Median	Min	Max	Number of measurements	
Fosa		**January 7, 10, 24**				
T [°C]	4.87	5.20	1.00	8.10		
SEC_{25} [µS·cm^{-1}]	79.0	86.7	26.8	119	26	
pH [-]	7.84	7.85	7.11	8.50		
Siodło II		**January 7, 10, 24**				
T [°C]	0.77	0.60	0.10	2.00		
SEC_{25} [µS·cm^{-1}]	81.5	82.9	61.1	99.0	6	
pH [-]	8.91	8.94	8.36	9.26		
Petrel		**January 13**				**A**
T [°C]	3.72	3.80	1.30	6.70		
SEC_{25} [µS·cm^{-1}]	99.7	53.7	43.0	290	5	
pH [-]	7.53	7.43	6.86	8.47		
Ecology		**February 1**				
T [°C]	2.81	3.15	0.10	6.70		
SEC_{25} [µS·cm^{-1}]	116	115	28.1	232	8	
pH [-]	7.67	7.78	7.23	7.97		
Vanishing		**February 1**				
T [°C]	3.42	3.40	1.40	5.50		
SEC_{25} [µS·cm^{-1}]	88.8	95.2	49.2	110	5	
pH [-]	7.91	7.81	7.70	8.17		
Czech		**February 7**				
T [°C]	3.40	3.40	1.70	4.20		
SEC_{25} [µS·cm^{-1}]	135	137	73.0	169	9	
pH [-]	7.61	7.64	7.18	7.89		
Ornithologists		**February 7**				**B**
T [°C]	4.72	4.90	1.60	7.00		
SEC_{25} [µS·cm^{-1}]	180	167	120	244	6	
pH [-]	6.70	6.94	5.26	8.11		
Petrified Forest		**February 2**				
T [°C]	2.93	2.30	1.00	6.20		
SEC_{25} [µS·cm^{-1}]	230	202	171	382	15	
pH [-]	7.99	7.93	7.44	8.95		

Analysing the spatial distribution of conductivity in the studied waters, the lowest SEC_{25} values (26.8-61.1 µS·cm^{-1}) was found in Siodło II Creek and Fosa Creek at points FL3, F4 and F8, and in Ecology Creek at points E1-E3, i.e. the measurement sections closest to the Baranowski and Ecology glaciers' fronts (Fig. 1, Fig. 4A). Higher SEC_{25} values (79.0-382 µS·cm^{-1}) in the catchments fed with glacial waters were recorded in the upper part of the Fosa Creek catchment (in the waters of Ginger Lake and Upper Lake and in Fosa Creek), in Ecology Creek at points E4, E5, E8, EL6 and EL7, and in Petrel Creek at

point PtL5. Points marked "EL" represent lakes in the paraglacial zone, which are fed not only by rainwater but also by melt water from dead ice and buried ice in fresh moraine deposits. Points E4, E5 and E8 in the Ecology Glacier forefield were small streams flowing out from these lakes.

The recorded pH values indicated that the majority of analysed aquatic environments in the area are either neutral or slightly alkaline (Fig. 4). However, pH at the measuring points in Siodlo II and point PL1, which constitutes a small lake in the upper part of the Petrified Forest Creek catchment, reaches values close to 9, indicating that the waters are more strongly alkaline (Table 2, Fig. 4).

Based on the analysis of the Pearson correlation matrix (Table 3), there was a statistically significant positive correlation ($p < 0.05$) between SEC_{25} and altitude. The obtained result was probably related to low SEC_{25} values in the Fosa creek system and high values in the Pertified Forest creek, which both represent the largest number in the data set (Table 2). First mentioned group of measurement points was located mainly at low altitudes, whereas second group was located along south-east slopes of the Panorama Ridge and is characterized by higher altitudes. Moreover, the Fosa creek system was fed mostly by glacial inflow against to the Petrified Forest creek, which is fed by the melting of snow cover, buried ice and permafrost mostly. The analysed dataset showed no correlation between pH and SEC_{25}.

Figure 5 is a biplot of pH against SEC_{25}. As the spread of points shows, the examined watercourses exhibit a characteristic relationship between pH and SEC_{25}. Waters fed by glacier ablation are grouped in an SEC_{25} zone not exceeding 100 $\mu S \cdot cm^{-1}$ (zone I in Fig. 1) while waters in catchments without glacial supply, which at the same time have been functioning in periglacial conditions for longer, are in the SEC_{25} range of 100-250 $\mu S \cdot cm^{-1}$, with only a few exceptions above these values (zones I and II in Fig. 5). Moreover, samples that represent relatively early deglaciated catchments (Petrified Forest creek, Czech creek, Ornithologists creek) differ in term of pH/SEC_{25} relation (III in Fig. 5) against direct glacier forefields area (I and II). The widest spread of SEC_{25} values is for the forefield of Ecology Glacier, with values ranged from 28.1 to 232 $\mu S \cdot cm^{-1}$. In terms of pH, Siodlo II was clearly distinguished for having the highest values (the most alkaline of the researched waters) and Ornithologists Creek for having the lowest (the most acidic). Last mentioned creek, especially its mouth section was place of is the place of existence of the Antarctic birds (penguins, skuas), southern elephant seals. Moreover, this part of creek catchment was cover by patches of mosses.

Table 3

Values of Pearson's correlation coefficient, r calculated based on complete datasets of measurement points. Statistically significant correlation are given in bold ($p < 0.05$)

	T	*SEC*	pH	*h*
T	1.000			
SEC	0.108	1.000		
pH	−0.189	−0.118	1.000	
h	0.005	**0.447**	0.026	1.000

T - temperature, *SEC* - conductivity, *h* - altitude

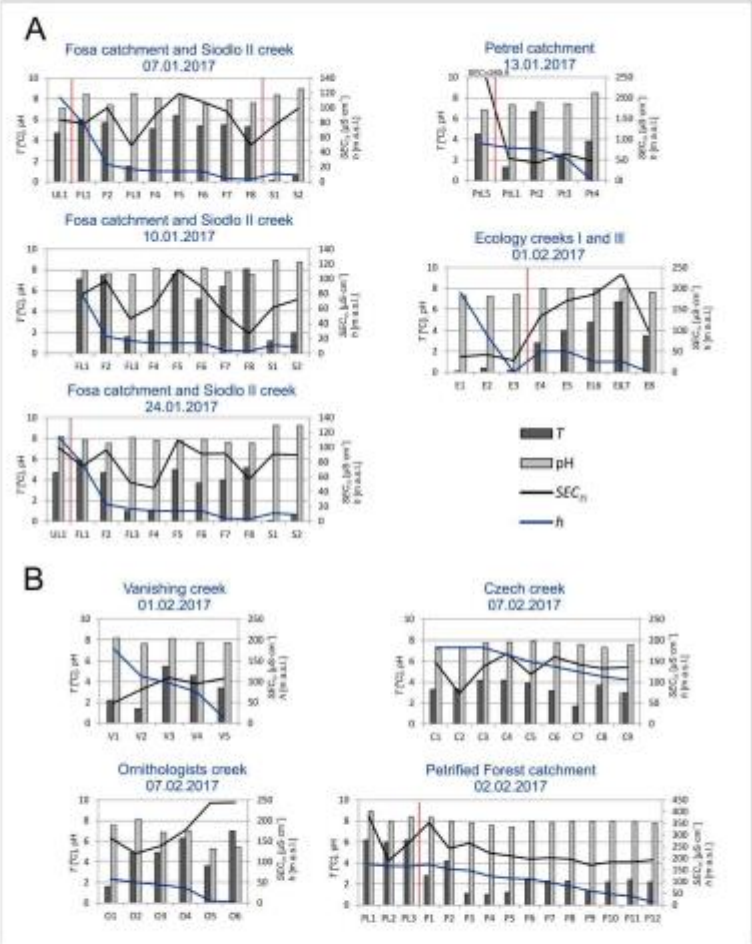

Fig. 4. T, SEC_{25} and pH values at the background of the longitudinal profiles of measured points: A - catchments with glacier-melt supply of creeks, B - catchment without glacier-melt supply of creeks. Red lines separate differ creeks' fluvial systems, and also lakes that are not include into fluvial systems. Samples UL1, PTL5, PL1-PL3 represent lakes without connection with surface drainage systems. Other 'L' samples represent lakes which are part of the surface drainage systems

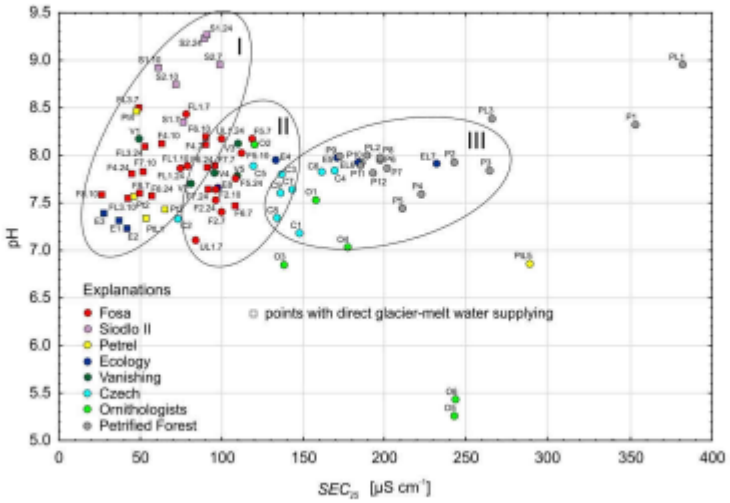

Fig. 5. Biplot of SEC_{25} and pH of investigated waters at the western shore of Admiralty Bay (numbers of points corresponds to Fig. 1). I-III - explained in the text

Discussion

The periodic intense inflow of ablation water has combined with morphological changes in the glacier front to cause significant variability in the drainage network, both spatially and temporally. In the course of field measurements performed in 2017 along the analysed watercourses, a cascade system of longitudinal profiles was observed. Sections of low longitudinal slope and considerable width coexist alternately with sections featuring high longitudinal slopes. In the first type, small shallow lakes may occur periodically, but in the second, steps or waterfalls often exist (Fig. 4). Studies of the chemical properties of waters at the western shore of Admiralty Bay to date have mainly been carried out in the mouth sections of watercourses [23, 25, 38]. The SEC_{25} results from measurements made for this work are similar to other authors' results for stream-mouth sections, and show generally lower values for glacially fed catchments and higher values in non-glaciated catchments, while the highest are in zones under the direct influence of aerosols or exposed to periodic influxes of sea waters. Works by Nedzarek and Pociecha [20] and Nedzarek et al. [22] presenting selected chemical variables for lakes and flowing waters in the Arctowski Oasis (at a different distance from the Admiralty Bay coast), showed that increases in SEC_{25} accompanied increases in concentrations of the tested ions of Cl^-, Na^+ and SO_4^{2-} that generally dominate in the ionic composition of waters in this area [21, 25]. Furthermore, the SEC_{25} in the results obtained by Nedzarek and Pociecha [20] show the largest fluctuations over time in lakes close to the bay shoreline and those in range of penguin colonies. SEC_{25} values in waters further from marine influences fluctuate less over

time. Research conducted in 2017 shows that the maximum instantaneous SEC_{25} values in summer (Fig. 4) in waters remote from the ocean's influence were recorded in small lakes in the very young moraine zone (290 $\mu S \cdot cm^{-1}$ at point PTL5 near Petrel Creek) and in the non-glaciated catchment of Petrified Forest Creek (382 $\mu S \cdot cm^{-1}$ at point PL1) (Table 2). Obtained values are higher than presented in previous studies of surface waters in this area [20, 22, 25]. It is difficult to clearly determine the difference in conductivity between previous research and those presented in this article. Measurements were taken in any case during austral summer (January-February). In 2017, it was found that Petrified Forest Creek is fed by melting snow cover and permafrost [39]. In addition, processes associated with permafrost such as solifluction, cryoturbation have an impact on the water chemistry in this creek [38, 40-42]. When comparing SEC_{25} values, it is worth considering the aspect of increasing the drainage network over the years due to the increase in the depth of the permafrost active zone. This theory is not unequivocally confirmed in the literature, although Kejna et al. [10] observed that the climate conditions on King George Island are characterized by annual variability due to the interaction of ocean, sea ice and atmosphere. It is possible that due to climate change permafrost in this area, among others Petrified Forest Creek degrades and the thickness of the active layer increases. Higher SEC_{25} values have only been registered by Zwolinski [38] in the mouth sections of marine-influenced watercourses during the winter thaw (with the activation of significant amounts of ions accumulated in snow cover). In the upper course of the Petrified Forest catchment, the high SEC_{25} value of 353 $\mu S \cdot cm^{-1}$ was recorded at point P1, where water is observed to flow in this period from sediments to the surface in the main channel of the watercourse. Further down the course the flow ceased, only to reappear as small outflows from sediments at points P3 and P4 and again as a larger outflow in the main channel at point P5. The low water temperatures recorded at these points (Fig. 4) attest to the possibility of water being supplied from the melting of permafrost and/or buried lumps of dead ice. Similar water temperature drops along the course of a stream accompanied by changes in SEC_{25} values were also recorded along the course of other streams in non-glaciated catchments - in Czech Creek and Ornithologists Creek (Fig. 4). Changes in the temperature and conductivity of water occurred in sections with changes of slope in the longitudinal profile, which could be associated with a change in how the watercourses are being fed. A similar phenomenon was also recorded in the glaciated catchment of Petrel Creek where there was a levelling of the longitudinal profile of the creek and thaw-type depressions periodically filling with water (point Pt3). The aforementioned watercourse sections, in which changes in both water temperature and conductivity indicate changes in the nature of supply, also feature pH values changing along the longitudinal profile (Fig. 5). At the same time, taking into account the studied water parameters that were steadiest while the 2017 measurements were being taken, lower pH values were recorded in Ornithologists Creek (points O5 and O6, Fig. 4) as compared to previously reported pH values [20, 22, 25]. Animals living near Arctowski Station have a significant impact on the chemical properties of water [25]. It has been proven that seabirds living in polar areas transport biogenic compounds to land [24], which means that the water is in around Antarctic birds (e.g. south polar skua; Adelie, gentoo and chinstrap penguins) can be enriched with phosphorus and nitrogen [43]. In addition, the chemical status of the water in this section of the creek is shaped by the ornithogenic soils and penguin guano, which accounts for the slightly acidic condition of the water [25, 44]. Droppings of the mammals (e.g. southern elephant seals and Weddell

seals) living in the area where physicochemical measurements were taken are a source of NO_3^- in freshwater [25].

It is also worth noting that based on measurements and analyses of flowing water samples from Arctowski Oasis from January-March 2005 (measured and sampled twice weekly) by Nedzarek et al. [22], Cl^- and Na^+ contents are higher in upper courses of the Czech Creek, Vanishing Creek and Petrified Creek as compared to the stream-mouth profiles. Based on analyses of soil samples, the authors concluded that Ca, Mg, K and Na contents increase with height above sea level. The SEC_{25} and water temperature measurements in watercourses taken for the present study, together with field observations, indicate, however, that the spatial variation in concentrations of components associated with atmospheric transport may be greater than indicated by Nedzarek et al. [22]. These components accumulate in snow and ice, and migrate towards the bottom of the cryogenic layer [38, 45, 46]. It can therefore be assumed that local depressions are sedimentation traps for sediments and chemical elements. Fine-grained deposits may accumulate from sedimentation *in situ* (on the surface, in the snow cover), along with chemical components that accumulate partly as a result of their greater possibility of binding with small fractions. Moreover, sediments and chemicals may also be related to runoff as the snow cover on the surrounding slopes melts, or to runoff of meltwater from buried ice and/or permafrost. Fragments of buried ice exposed by surface erosion and linear erosion were observed in the analysed catchment areas, both glaciated and non-glaciated.

The basic physicochemical water parameters of paraglacial areas are highly variable over time, as a result of changing weather conditions. These conditions affect the flow of both matter and energy, and affect the pace of snow cover melting and glacier ablation. Previous studies have indicated increased SEC_{25} and ion concentrations during the Antarctic summer in non-glaciated catchments. This is related to the declining share of snowmelt waters, raising the proportion of infiltration waters and waters originating from ground-ice melting [22, 25, 38]. In the glacial catchments during the summer season the amount of suspended matter in the watercourses increases, but the proportion of ions decreases, which reduces SEC_{25} values. The repeated measurements in the summer of 2017 on the forefield of the Baranowski Glacier clearly indicate a relationship between SEC_{25} values and glacier ablation intensity. At points F8, S1 and S2, an increase in SEC_{25} was observed on January 24 (Fig. 4), which may be associated with a reduction in the proportion of ablation water in the creeks' flows. Decrease in glacier ablation was observed due to a drop in air temperature in the days preceding measurement (Fig. 2).

The conductivity results for samples from Spitsbergen vary depending on the region of the island. It was found that in samples collected from the Revelva catchment located in the vicinity of the Polish Polar Station, Hornsund, the values in July 2015 ranged from 35.0 to 80.1 $\mu S \cdot cm^{-1}$, and in September 2015 56.0-135 $\mu S \cdot cm^{-1}$ [47]. In turn, the value range of this physicochemical parameter in Tyvjobekken and Reindeer Creek, located in the NW part of the Wedel-Jarlsberg Land, in the Bellsund region of Spitsbergen was higher and ranged from 196 to 342 $\mu S \cdot cm^{-1}$ [48]. Waters taken from these streams had a pH of 7.26 to 8.18. In addition, water samples taken from the Scott River in NW Wedel Jarlsberg Land (SW Svalbard) had a conductivity of 66.3-169 $\mu S \cdot cm^{-1}$ and a pH of 7.41 to 8.79 [49]. For comparison, the results of conductivity samples of water originating from Mellville Island, Nunavut, Arctic Canada ranged from 5.00 to 1230 $\mu S \cdot cm^{-1}$ in 2008 [50] and from 11.0 to 428 $\mu S \cdot cm^{-1}$ in 2009 [51]. The upper limit of the value in 2008 is more than twice higher than the highest value of conductivity in water samples from King George Island.

The authors of the article [49] showed a large impact of sea spray on water samples with the highest conductivity. The average pH was 7.80 in 2008 [50] and from 7.43 in 2009 [51]. These results are close to the average pH values of the water samples described in this article. Studies of water taken from the Chena River, Alaska have shown that their average conductivity is 192 $\mu S \cdot cm^{-1}$ and pH 7.35 [52].

Conclusion

The pH, SEC_{25} and water temperature measurements taken in a dense network of measurement points along watercourses and in lakes on the western coast of Admiralty Bay show that the variability in the determinants of water chemistry is greater than previously suggested. The parameters used in the research provide only limited information on the possible variation in concentrations of ions and spatial changes in the supply structure of water bodies. However, the study has the undoubted advantage of requiring only a relatively modest investment of time and money. It may therefore support the selection and verification of measurement points and interpretation of results of detailed chemical analyses.

The measurements conducted, which indicate a high variability of T and SEC_{25} along the watercourses, suggest some sections of the watercourses being more heavily fed by waters from the melting of buried ice of various origins (including permafrost). Analysis of the obtained data confirmed that the waters fed by glacial ablation have SEC_{25} up to 100 $\mu S \cdot cm^{-1}$. Waters in catchments without glacial supply that were longer under the influence of periglacial conditions had SEC_{25} within 100-250 $\mu S \cdot cm^{-1}$. In addition, statistical analysis showed that samples taken from areas in the early deglaciated catchments (Petrified Forest Creek, Czech Creek, Ornithologists Creek) are characterized by a higher pH/SEC_{25} ratio compared to water samples taken from the forefield of the glacier. These results testify to the significant impact of soil background (geochemical factor) and glacier retreat on the formation of surface water chemistry on the western coast of the Admiralty Bay. In addition, it was found that Siodlo II had the highest pH values (the most alkaline) and the lowest Ornithologists Creek (the most acidic). Considering the location of large numbers of birds and pinnipeds colonies around Ornithologists Creek, the obtained pH values may indicate significant impact on the chemical properties of water. The large variability of the measured parameters in the upper and middle courses of the streams suggests that the geochemical system of non-glaciated areas on the western shore of Admiralty Bay can only be fully understood with testing using a larger number of sampling points. At the same time, the measured parameters showed a high sensitivity to short-term fluctuations in weather conditions affecting changes in the structure of water supply, which indicates the need for frequent sampling. Such sensitivity of aquatic ecosystems to weather conditions can also affect the variability of other chemical substance concentrations.

The remarkable remoteness of the research area, and the number of samples being limited by the ability to store them in a frozen state at the station and deliver them to the laboratory in Poland, lead us to conclude that it would be a good solution to furnish the H. Arctowski station with equipment to conduct complex chemical analyses on site. The remote transport of samples poses a risk of changes in both the physicochemical parameters being measured and the concentrations of certain compounds, due to possible temperature changes and highly volatile compounds transitioning to the headspace phase.

Extending the chemical laboratory at the Polish Polar Station would increase its scientific potential and thus enable the expansion of international cooperation.

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7.2 Verification of detailed hypothesis 2: Water–sediments–snow interactions influence pollution transport and distribution in the study area

Until recently, information on the sources of chemical pollutants and factors influencing the chemistry of waters and sediments in Antarctica was scarce in the available literature. However, due to the fast pace of climate change, scientific interest in this subject is growing. The research carried out as part of the doctoral dissertation is extremely important in determining the condition of the aquatic environment in terms of the presence of selected chemical species, including pollutants. In addition, sediments were also investigated, which, together with the aquatic environment results, can be a valuable source of information on the correlation between these matrices, the migration of chemical compounds between them and the environmental fate of pollutants.

Previous studies have proven that some persistent organic pollutants (POPs), including polycyclic aromatic hydrocarbons (PAHs) have been proven to exist in Antarctica in both animate and inanimate elements of nature [1,6,11]. Identifying the sources of these compounds is a challenge for scientists, because they can be anthropogenic and of natural origin. The primary sources of PAH emissions are: incomplete combustion of biomass, fossil fuels, oil spills and diagenesis of organic matter [3,12,84]. The atmospheric circulation contributes to PAHs distribution in the research area. These chemical compounds find their way into various elements of the Antarctic environment from the Southern Hemisphere, as a result of dust transport and cyclic volatilisation / deposition processes [85].

Attention should be paid to the toxicity, mutagenicity and carcinogenicity of PAHs [35]. Moreover, they have a tendency to bioaccumulate in the environment [29]. The properties of these chemical pollutants make exposure to them in the Antarctic environment a particular threat to Antarctic fauna and flora [8,9].

Apart from direct sources, the processes occurring at the snow and firn surface have an impact on the environmental fate of chemical pollutants in Antarctica. Their metamorphic processes depend on temperature fluctuations. When grain growth occurs, this increases the firn permeability, and contaminants are transferred to the deeper layers, which can cause increased accumulation of chemical pollutants in the cryosphere, leading

to them being trapped in polar areas and creating long-term hazard conditions [86]. As part of checking detailed hypothesis 2, the research presented in **publications IV–VI** included herein was carried out.

The verification of the second detailed hypothesis is presented in the article: **Potapowicz J., Szumińska D., Szopińska M., Bialik R.J., Machowiak K., Chmiel S., Polkowska Ż., Seashore sediment and water chemistry at the Admiralty Bay (King George Island, Maritime Antarctica) – geochemical analysis and correlations between the concentrations of chemical species, *Mar. Pollut. Bull.*, 152 (2020) 110888 [publication IV]**. The article presents a detailed analysis of the concentrations of selected chemical species in water and sediment samples taken from the profiles of the watercourses (from the source to the mouth), including standing water (the lake and shore zone of Admiralty Bay). Therefore, a detailed study of the seashore area allowed us to observe the possibilities for potential discharge of the analysed elements and ions into Admiralty Bay. An attempt was also made to interpret the spatial distribution of selected metals, other chemicals and parameters in waters and sediments, as well as their possible mutual correlations.

Principal component analysis was used to understand the relationship between individual chemicals and the physicochemical parameters in the catchments on the western coast of Admiralty Bay during two research periods (the first at the beginning of January and the second at the end of March of the austral summer 2016). Samples were taken from the forefield of the Ecology, Sphinx and Baranowski glaciers, from the seashore (seawater from the coastal zone near Arctowski Station and the Sphinx forefield zone, and water from the bays in the forefields of the Ecology and Baranowski tide glaciers), as well as from Ornithologists Creek and the lake fed by Moss Creek. This analysis was carried out using a set of selected variables: pH, conductivity, total organic carbon concentrations, selected trace elements (Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr , Ag, Cd, Cs, Ba, La, Tl, Pb), as well as the concentrations of individual anions (F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). Based on the obtained results, the analysis of geo-accumulation index (I_{geo}) calculated for

soils collected in study area was also made. The obtained research results have been discussed in detail in the attached publication.

Based on the performed study, it was found that physical weathering has resulted in higher concentrations of Fe, Ni, Co, Al. In addition, the acidification effect of the sediments was seen in, for example, higher phosphate concentrations in March. The consequences of this may be increased leaching of exchangeable bases, mineral transformations and increased release of metals such as Fe and Al. The determinations of chemical compounds and the analysis of the geo-accumulation index found that concentrations of Cd and Pb are increased in the vicinity of the station, which may be the result of anthropogenic activity. Moreover, organic matter in this area may also be a secondary source of these metals, since they may be accumulated by vegetation and are rarely found in rocks of the basalt/andesite type.

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Seashore sediment and water chemistry at the Admiralty Bay (King George Island, Maritime Antarctica) – Geochemical analysis and correlations between the concentrations of chemical species

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ABSTRACT

This study covers water and sediment chemical characteristics by the western shore of Admiralty Bay (King George Island, Antarctica) in 2016. Chemical processes between sediment and water have been described based on the determination of ions, metals, non-metals, and TOC concentrations. Rock weathering is an important source of Fe, Ni, Co, Al in the seashore area. The PCA shows the impact of acidification in the release metals from sediment. Our results indicate that riverine mineral fluxes need to be accounted for as the volume of melt increases in response to climate change. Based on geoaccumulation indexes (anthropogenic fingerprint), we observed an increased concentration of Pb (I_{geo} = 1.643), in the lake near station facilities and Cd in the area of Ecology Glacier (I_{geo} > 1.389). Taking into account climate change and the intensification of anthropopressure, our study indicates that Antarctica requires a special focus on the seasonal dynamics of mineral content and pollution assessment.

1. Introduction

It is estimated that only about 0.5% of the Antarctic emerged surface is free of ice in the summer, but as a result of the occurrence of fluvial drainage systems the landscape and chemistry of different parts of environment can undergo significant changes (Baroni et al., 2005; Mink et al., 2014). Moreover, recent studies show that the periglacial zone is one of the most rapidly changing areas of the world (e.g. Cooper et al., 2011; López-Martínez et al., 2012; Karlsson et al., 2012, 2015; Oliva and Ruiz-Fernández, 2017; Ravanel et al., 2017; Oliva et al., 2018). As a result of rapid glacier retreat, the new ice-free zone with a varied morphology (Szilo and Bialik, 2018) and a different rate of chemical weathering (Szopińska et al., 2018) is shaped at the western shore of the Admiralty Bay, similarly as in the other parts of the Antarctic region (Oliva and Ruiz-Fernández, 2017). It has been proven (Bockheim et al., 2013) that permafrost processes have taken place more intensively in the last decades because of a high intensity of the deglaciation. The presence of permafrost as well as the physical weathering and the cryogenic processes (generally through freeze-thaw cycles) have a significant impact on the formation of initial soils in South Shetland Islands (Navas et al., 2005, 2008; Schaefer et al., 2008; López-Martínez et al., 2012).

Most of all, climate change causes also the increase of the surface runoff, which results in the transfer of larger amounts of mineral and a little of organic matter to the fresh water in the Antarctic area (Szopińska et al., 2018). As a consequence the attachment of mineral and organic matter to circulation in the environment, the transformation of surface and aquatic sediments occurred (López-Martínez et al., 2012; Oliva and Ruiz-Fernández, 2017). The deglaciation leads to an increase in transport of matter between land and water. The inflow and blowout of mineral and organic matter from the land increases, which causes hydrobiological changes in the individual elements of the environment, e.g. coastal waters or soil (e.g. Cabrerizo et al., 2012, 2013; Klánová et al., 2008; Potapowicz et al., 2019; Szopińska et al., 2018).

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As a result of reducing the transparency of the water, it comes to changes in primary production and increasing the process of sedimentation of mineral matter to the bottom.

A consequence of the global warming is increasing of ice-free surface areas with rock formations exposed to weathering. Chemical weathering of basic igneous rocks occurs when sufficient moisture is available, especially in the form of thin films of salt solutions with a low freezing point (Claridge and Campbell, 1984). Hence, in this work, near shore sediment and water samples have been analysed, as they are particularly exposed to this type of processes. This study focuses on the analysis of compounds belonging to various groups of inorganic chemicals (heavy metals, basic ions, e.g. SO_4^{2-}) in various parts of the abiotic environment (surface waters, sediments) in the near shore area, and in such combination this has never been conducted in the area of Admiralty Bay. Recently, factors shaping the chemistry of flowing water in this area have been analysed (Szopińska et al., 2018; Szopińska et al., 2019). In the cited studies, samples from several watercourses of glaciated and non-glaciated catchments were included. However, the mentioned research did not focus on the analysis of estuary sections of these systems, and apart from the waters in the mouth profiles of the watercourses, also the standing water (the lake and the shore zone of the Admiralty Bay) has not been analysed. Therefore a detailed study of the seashore area allowed us to observe the possibilities for potential discharge of the analysed elements and ions into the Admiralty Bay. The achieved research goals will allow to broaden the knowledge on the spatial distribution of heavy metals and other chemicals in various components of the seashore environment, as well as their possible mutual correlations.

2. Material and methods

2.1. Study area

The sampling area is located by the western shore of the Admiralty Bay (King George Island, South Shetland Islands, Antarctic Peninsula). South Shetland Islands region is characterized by a moderate thermal range, which is accompanied by summer rains and high cloudiness. In addition, the climate is cold and maritime (Schwerdtfeger, 1970; Simonov, 1977; Vaughan et al., 2003). The King George Island has an area of about 1400 km^2, making it the largest island in the South Shetland Islands. Its area is < 5% free of ice during the summer, but generally it is glaciated (Simões et al., 1999; Almeida et al., 2017). Study area (western shore of Admiralty Bay) includes the Antarctic Specially Protected Area 128 (ASPA No. 128) which was established mainly due to the presence of a unique set of birds and marine mammals. ASPA No. 128 is located south of the Henryk Arctowski Polish Antarctic Station and east of the Warsaw Icefield.

2.2. Sampling

Water and sediment samples were collected twice during the austral summer of 2016. The first sample series (I) has been collected at the beginning of the summer, in January, when the snow cover was significantly reduced, while the second series (II) was collected in March 2016, at the end of the summer season. Samples were taken from the forefield of glaciers: Ecology, Sphinx and Baranowski, the sea shore (sea water from the coastal zone near Arctowski Station and the Sphinx forefield zone, and water from the bays in forefields of the tide glaciers – Ecologia and Baranowski), as well as from the Ornithologists Creek and the lake fed by the Moss Creek (Figs. 1, 2) (saline samples taken from the coastal zone of the bay are shown as red dot in Fig. 1). Detail information about sampling points are presented in Supplementary data.

The analysed water samples of 1 L volume were collected manually. Each polyethylene bottle was rinsed three times with the sampled stream or bay water at the collection site. After pH and conductivity measurements, water samples were frozen and stored at −20 °C. The sediment samples were collected manually into polyethylene bags. In order to carry out the analyses, it was necessary to take approx. 500 g of each sediment. The bags were sealed and stored at −20 °C. The person taking samples of water and sediments wore gloves to avoid contamination. All samples have been shipped frozen to Poland (−20 °C).

2.3. Laboratory methods

A DIONEX 3000 chromatograph (DIONEX, USA) was utilised for inorganic ions determination. A conductometric detector was used during both analyzes. Dionex IonPac AS22 analytical column was used in the analysis of anions (eluents: 4.5 mM Na_2CO_3 and 1.5 mM $NaHCO_3$, flow rate: 0.3 mL min^{-1}). The determination of cation concentrations was obtained using Dionex IonPac CS16 analytical column (eluent: 38 mM methanesulfonic acid, flow rate: 0.36 mL min^{-1}).

Supernatants obtained as a result of prior preparation of sediment samples and water samples have been analysed using a catalytic combustion method with non-dispersive infrared detection (NDIR) on the TOC-VCSH/CSN Analyzer (SHIMADZU, Japan).

Specific electrolytic conductivity (SBC_{25}) and pH of water samples were measured with a Cx401 (Elmetron, Poland) multi-functional measuring device immediately after sampling. The pH of extracts from sediments has been measured in the extract using the multi-parameter inoLab® Multi 9310 device.

Water samples as well as mineralized and diluted extracts of sediments samples were analysed using Thermo XSERIES 2 ICP-MS inductively coupled plasma mass spectrometry featuring 3rd generation collision cell technology with kinetic energy discrimination (KED) (Thermo Fischer Scientific, Germany). During the analysis the device worked with the following parameters: collision gas (Ar) flow: 13 L min^{-1}, auxiliary gas flow: 0.7 L min^{-1}; nebuliser gas flow: 0.9 L min^{-1}, collision cell technology (CCT) gas (8% Hydrogen in Helium) flow 5.5 mL min^{-1}.

Water samples have been handled with special care to avoid cross-contamination. The determination of pH, SBC_{25}, ions, elements and TOC in water samples has been provided using the aforementioned equipment, too. Precision errors for the ions, all elements and TOC analyses were 5% according to repeat analyses of mid-range standards, while the detection limits are listed in Table 2 in Supplementary data. No contaminants were detected above this limit in the analyses of blank deionised water samples. Detailed preparation of samples before the analysis is described in Supplementary data.

2.4. Statistical analysis

Pearson's correlation coefficients (r) were calculated using Excel 2010 (Microsoft Office, version 2010, U.S.A.). This allowed the detection of pair-wise relationships among the trace elements and TOC concentration in water and sediment samples. Statistical significance of the correlation coefficients was assessed at a significance level of $p < 0.05$, and verified using the t-Student test. On the basis of the results obtained for selected metals, the geoaccumulation index (I_{geo}) for sediment samples was calculated. The sample 6.2 was used as a reference point in this calculation. The lowest metal concentrations were found in this point, due to its largest distance from the Station. In March, the concentration of Cd at 6.2 (II) was below the limit of detection (< LOD), so for the content of this element, point 6.1 (II) was used as background.

The geoaccumulation index, by means of which the degree of anthropopressure can be determined, was proposed by the German scientist Müller (1981) from the University of Heidelberg. The geoaccumulation index method is a quantitative indicator of the degree of heavy metal pollution in sediments. The index is calculated as follows:

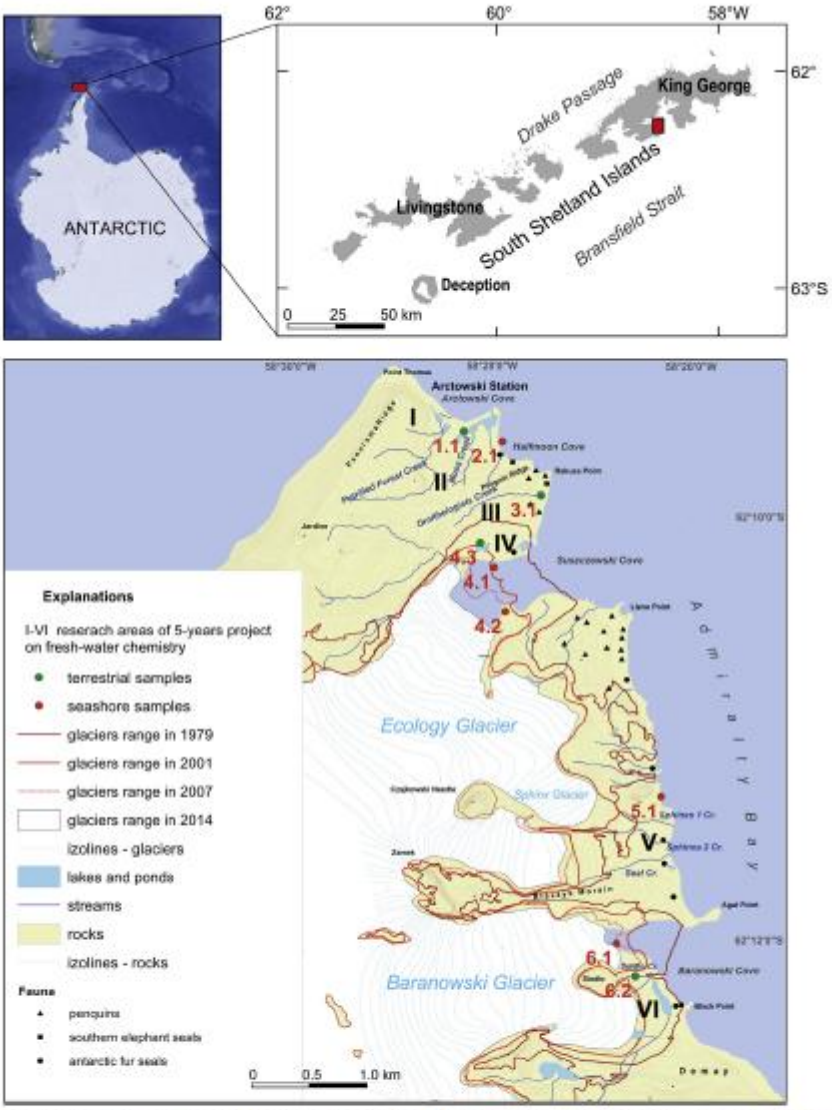

Fig. 1. Map of the western shore of Admiralty Bay (Maritime Antarctica) showing glaciers' retreats between 1979 and 2014 and the location of the sampling points and (prepared based on Pudełko, 2008; Landsat image LC82181032014016LGN00 obtained from www.usgs.gov; GoogleEarth application). Freshwater sampling points are marked in green and seawater in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$I_{geo} = \log_2 \frac{C_n}{1.5\, B_n},$$

where:

Cn, Bn - element concentration in the sample and background, 1.5 - correction factor, which is used to eliminate the natural fluctuations (Lu et al., 2012).

This method determines the degree of heavy metal pollution by assigning it an appropriate class. As a final data processing stage, a principal component analysis (PCA) was calculated using MATLAB Version: R2013a with Statistics Toolbox Version 9.1 manufactured by MathWorks, U.S.A.

Fig. 2. Measuring points of the studied creeks and forefields of glaciers at the western shore of Admiralty Bay. Freshwater sampling points are marked in green and seawater in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results

3.1. Basic chemical measurements

The values obtained as a result of physicochemical measurements (pH, conductivity), as well as the determined concentrations of ions and total organic carbon for water and sediment samples, were placed in Tables 3 and 4 in Supplementary data, respectively. The pH values for surface waters ranged from 6.74 to 9.38 in January and from 6.28 to 8.20 in March. In turn, the pH of sediments from the western coast of the Admiralty Bay ranged from 6.37 to 9.16 in January and from 5.34 to 8.69 in March. In both types of samples higher values (> 8 in terms of water and 7.22–9.17 in terms of sediments) of pH characterized samples related to saline environments (samples no 2.1, 4.1, 4.2, 5.1, 6.1).

In the case of electrolytic conductivity of water, the values were in the range of 40.9–47,000 μS/cm in the summer season, and the sediment conductivity ranged from 55.5 to 2680 μS/cm. One should note that the highest conductivity characterized water samples (8300 to 47,000 μS/cm) and sediment samples (449 to 2680 μS/cm) collected in saline environment. Among terrestrial samples the mouth section of the Ornithologists creek (sample 3.1) is characterized by rapid changes in conductivity, comparing the beginning and end of the summer season (from 113 μS/cm to 2105 μS/cm in March). Similarly, high increase in conductivity were observed in sediment sample 4.1 (Admiralty Bay in front of Ecology Glacier) and water sample 6.1 (Admiralty Bay in front of Baranowski Glacier). Differences in the conductivity of individual samples are caused by different sources of supplied ions depending on the month with temporal strong influence of sea water (tides, waving) and glacier melt inflow. Due to the high salinity of water reservoirs from which water and sediment samples 2.1, 4.1, 4.2, 5.1, 6.1 were taken, these samples have higher conductivity values than samples taken from water reservoirs with low salinity. The salinity of the water reservoir may affect on concentration of sodium cations, chloride and sulphate anions, but this trend cannot be clearly confirmed for other chemical species.

On the basis of the obtained results (Table 2), it was found that both the sediments and surface waters were dominated by Cl^-, Na^+ and SO_4^{2-}. What's more, this proportion was preserved in January and March. However, one should note that in water samples of saline environments (2.1, 4.1, 4.2, 5.1, 6.1) chlorides, sodium and sulphates are dozen of times higher than in terrestrial samples. However, in terms of sediment samples there is no such a rule and particular terrestrial samples are characterized by higher content of this compounds compared to saline one (e.g. Cl- in sample 3.1 was 8.1 mg/L in March and was higher compared to samples 4.1, 4.2, 5.1 and 6.1). Taking into account other compounds it should be noted high content of bromine in water samples no 4.1 and 4.2 (65.5–87.7 mg/L) and calcium in sediment samples 4.3 and 6.2 (6.83–13.8 mg/L). Moreover, it is worth taking a closer look at the concentrations of ions that contain nitrogen (NO_3^-, NH_4^+) in their structure. The concentration of NO_3^- in the samples of surface water taken in most cases did not exceed the limit of detection. However, at the points 3.1 (I), 2.1 (II), 3.1 (II) and 6.2 (II), the content of these ions was determined, ranging from 0.14 to 1.33 mg/L. The above-mentioned points can be found in the following measuring areas: 2.1- Halfmoon Cove, 3.1- Ornithologists Creek, 6.2- forefield of the Baranowski Glacier. Attention should be paid to the concentration of NH_4^+ ions at the points: 2.1 (I), 4.3 (I), 5.1 (II), which were distinguished among the tested surface water samples by the ammonium concentration values above the limit of detection. The concentration of this cation at 5.1 (the forefield of the Sphinx glacier) was exceptionally high, amounting to 10.49 mg/L in March. In waters, there was a clear correlation between the occurrence of NO_3^- and PO_4^{3-}. The concentration of phosphate was above the limit of detection at the same measurement points as NO_3^- and ranged from 0.32 to 0.53 mg/L. This relationship was not visible in the case of sediments. The concentration of PO_4^{3-} in the tested sediment samples was in the range of 0.003–0.024 mg/g dry weight (dw) and in each case was

detected. The concentration of NO_3^- was from 0.001 to 0.081 mg/g dw and varied depending on the measurement period.

3.2. Trace metal and total organic carbon analysis

The total organic carbon (TOC) concentration in the surface water samples collected on the western coast of the Admiralty Bay ranged from 0.018 to 2.50 mg/L in January and from 0.016 to 4.09 mg/L in March. Lower TOC values were found in freshwater samples from King George Island (Szopińska et al., 2018), which may indicate that the water samples described in this article contain a relatively large amount of organic matter. For comparison, in the samples of sediments collected at the same measurement points, the TOC content was estimated at: 0.83–6.59 mg/g dw in January, as well as 0.72–4.19 mg/g dw in March. The highest values of TOC occurred in terrestrial as well as saline samples. However, it is worth to note that TOC values showed strong decreasing between January and March in samples collected in forefield of tide glacier Ecologia (samples 4.1, 4.2) and in forefields of Sphinx and Baranowski glaciers (samples 5.1, 6.1, 6.2). Moreover, in sample 2.1 collected in Halfmoon Cove, near the outlet of Ornithologists creek and southern elephant seals and penquins colonies the TOC value increased twice between January and March.

The results of trace metal analysis show that in the majority of the studied samples the total base metal concentration can be classified as low (Supplementary Table 5.). Based on the obtained data, relatively large amounts were found in saline water, e.g. boron, strontium, also rubidium, phosphorus. Szopińska et al. (2018) also noted the increased concentration of boron and strontium in freshwater, however, the results of the analysis of water and sediment samples described in this article are characterized by even higher concentrations. This tendency is especially visible in the case of waters. In addition, Table 6 (A. and B.) in Supplementary data shows the correlations between TOC and individual metals and non-metals separately for sediments and surface waters collected in the summer season. In the case of surface waters, a very strong correlation was observed ($0.8 < |r| \leq 1$) between Li and the following elements: B, Ga, Rb, Sr, Cd, Cs, Ba, Pb, as well as B and Ga, Rb, Sr, Cd, Cs, Ba. Similar relations also connect Al with Fe and Zn, Fe with Cu, Ga with Ag and Ba. Also noteworthy are the correlations between Sr, Cd, Cs, Ba and Rb, as well as Cd, Cs, Ba and Sr. Based on the obtained results, it was found that the occurrence of Cd, Cs and Ba is strongly related to each other.

In the case of sediments, strong correlations predominate ($0.6 < |r| \leq 1$), however, based on the obtained results, it can be concluded that Ni was strongly correlated with Li and Cr, as was La with Mn, Ga with Rb and Tl with Pb. It can therefore be estimated that metals and non-metals identified in surface waters taken from the western coast of the Admiralty Bay clearly show more statistically significant correlations than the chemical species present in sediments. In both matrices, no statistically significant relationship was observed between the TOC and any metal or non-metal.

3.3. Multivariate data analysis result

A PCA was performed separately for data from both water and sediments. In addition, all were investigated for the series from January, March and the combined data, as was already done by Szopińska et al. (2018). Fig. 3(A–C) shows that for all series of water data, the first principal component represents > 97% of the variance, and it had a strong positive correlation with Na^+, Cl^- and SO_4^{2-} (and had no strong negative correlations). The results of PCA are determined mostly of saline samples. In contrast to the water data, for both series of sediment samples, two principal components were identified (Fig. 4A–C). For January, first two PCs represent collectivity > 93%, while for March about 90% of the variance. For January, PC1 was strongly positively correlated with Al, while PC2 was strongly correlated with Fe and Na^+, and correlated negatively with Ca^{2+}. Although for March PC1 was also strongly positively correlated with Al, it was negatively correlated with Fe. Moreover, PC2 was strongly correlated with P and had no strong negative correlation. For the entire data set of soil, PC1 and PC2 represented 86% of the variance (Fig. 4C). PC1 was strongly positively correlated with Al and so was PC2 with Fe, but it was also negatively correlated with P. Fig. 4(A–C) clearly show the significant change in time of the sediment chemistry characteristics.

3.4. Geoaccumulation index (I_{geo}) analysis

The results obtained to determine the degree of heavy metal pollution are shown in Table 1. The calculated I_{geo} values were from −1.667 to −0.013 for Ni and − 11.711 to −0.1783 for Cr, suggesting that this area is not contaminated with these metals. The geoaccumulation indexes for Pb in almost all sediment samples from January (I) and March (II) were less than zero, which means that no contamination with this metal was found in these places. Only in the point 1.1 in March this index was 1.643. It can therefore be concluded that at the end of the summer season at the point from the lake at the Station there was moderately strong lead pollution. As for Cu, the indices ranged from −0.677 to 0.523, indicating no contamination or slight contamination with this metal. There was no leading trend in the presence of contamination with this metal, because the indexes changed depending on the period of sampling of sediments and values in particular points did not maintain the same level at the beginning and end of summer. On the basis of the geoaccumulation indexes calculated for Cd, it was determined that at the points: 4.2 (I), 4.3 (I), 3.1 (II) there occurred a heavy contamination with this metal. The situation was better at the point 3.1 (I), where moderate to heavy contamination with cadmium occurred, and at the points: 4.1 (I), 1.1 (II), 4.2 (II), 4.3 (II), which were moderately contaminated.

4. Discussion

4.1. The influence of natural factors on the chemical composition of water and sediment

Considering the geological structure of the studied areas I-III, in which the most dominant products are basalt and andesite lavas with intercalations of both fluvial desposits and the debris from mechanical weathering of these rocks (Birkenmajer, 1980, 1996, 2003; Birkenmajer et al., 1991) (Supplementary material S3), the main minerals there are: plagioclases (a source of Ca, as well as Na, Rb), pyroxenes and amphiboles, mainly hornblende (a source of Mg, Ca, Fe, Ti, Na, Mn, also Rb), less often olivine (if olivine basalt, a source of Mg and Fe, in a smaller amount of Cr, Ni), biotite (a source of Fe, Mg, K, in a smaller amount Rb, Li, B, Cs, Sr, Ti), phlogopite (source K, Mg, in a smaller amount Fe, Ti, Mn), volcanic glass (coming from mafic and intermediate volcanoes). All the primary minerals are also the source of Al and the SiO_2 released in the weathering processes (Polański, 1988). Secondary minerals, which are results of non-advanced chemical weathering in the conditions of cold climate (Lee et al., 2004) and the mineralization associated with hydrothermal metasomatosis, are clay minerals (smectite, illite, seladonite), zeolites, calcite, chalcedony, with slight Cu and Fe mineralization (Inoue, 1995). More detailed geological characteristics of the studied area are described in Supplementary material S3. Geological setting. Relatively large amounts in salty samples, e.g. boron, strontium, rubidium, phosphorus, probably result from the effect of secondary boron donation by illite in the processes of diagenesis. In addition, Szopińska et al. (2018) observed a strong correlation between Na^+, Cl^- and B, allowed to conclude that B in freshwater may come from sea spray. In this paper no such correlation was found, therefore we suppose that illite in the sediment binds boron into the inter-package structure. Therefore, saltwater reservoirs, which are characterized by a high content of illite, have higher boron concentrations in the sediment than in water. During diagenesis under the

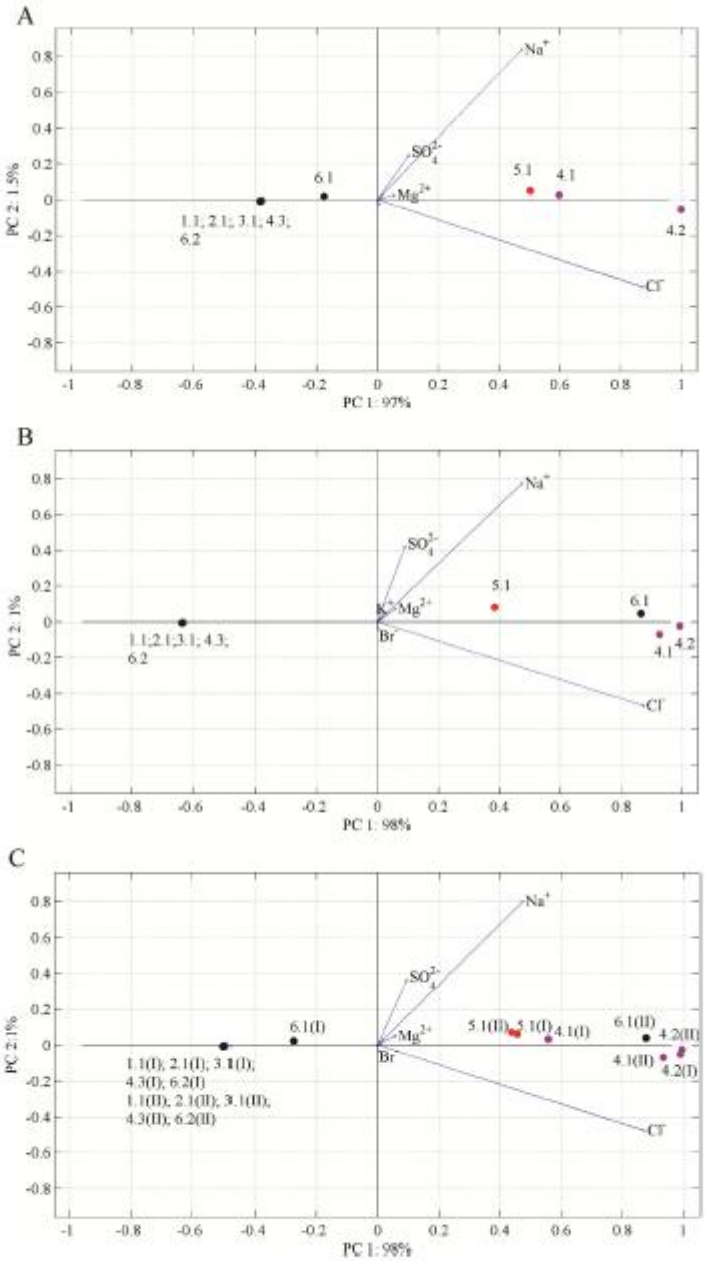

Fig. 3. PCA biplots for water series: A. data set for January; B. data set for March, C. entire data set (January and March).

ocean floor, illite in turn releases boron and then enriches ocean water. Phosphorus is also more concentrated in marine and oceanic than terrestrial environments. The exception is its local origin in the form of animal droppings, e.g. birds.

The chemical compositions of sediments at 1.1 and 2.1 essentially reflect the geological structure of the substrate. The high content of Fe, Ni, Co, and Al is typical for the mechanical rock weathering in this region (Birkenmajer, 1996). The samples contain slightly elevated

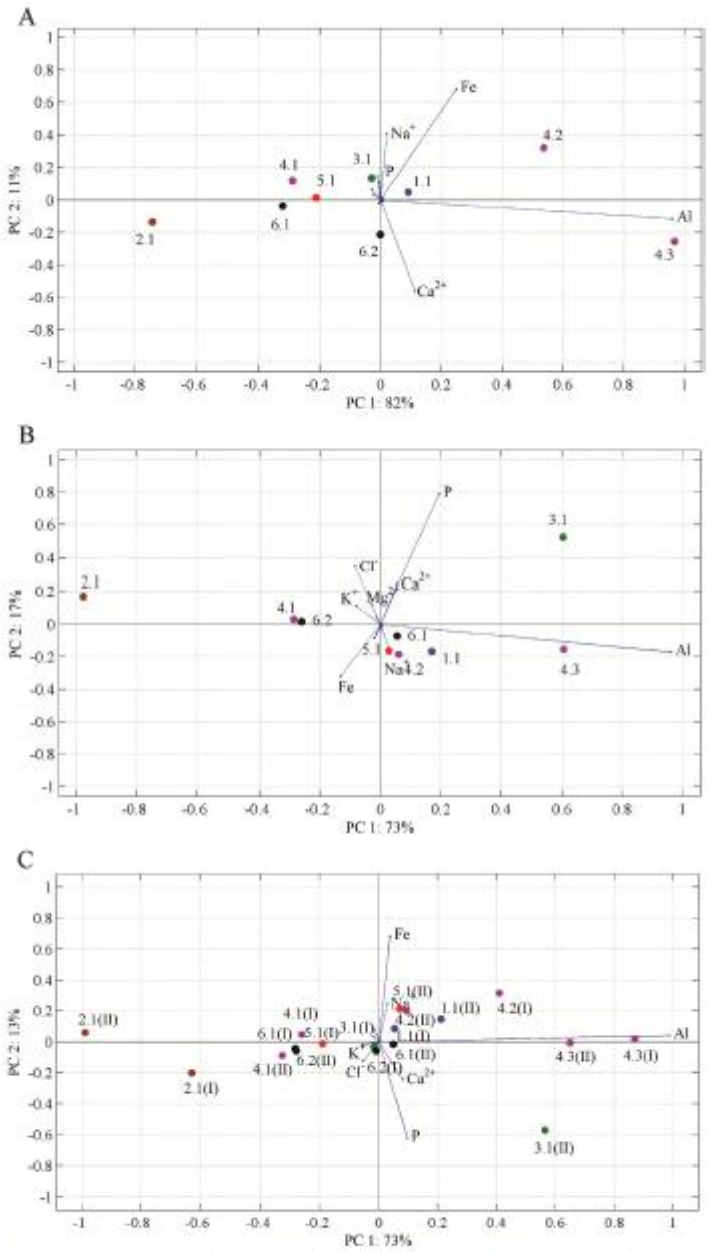

Fig. 4. PCA biplots for sediments series: A. data set for January, B. data set for March, C. entire data set (January and March).

content of elements, which may have their source not only in the parent rocks (eg. Zn, Ga, Pb, Na, Li, B, Ba, Rb, Cu). Hydrothermal solutions (highly mineralized aqueous solutions) may have been formed in several episodes related to local magma pulses in the region. Some of the elements are probably related to hydrothermal activity, the source of which was more acidic magma than the magma responsible for the formation of the local rocks. Rocks with an increased SiO_2 content are exposed on the surface in the area of Wegger Peak or Barton Penninsula (Lee et al., 2004), yet they may also occur deeper in the ground of the analysed area. The metasomatosis associated with the effects of

Table 1
The values of geo-accumulation index (I_{geo}) calculated for soils collected at the western shore of Admiralty Bay. As the background content of each element, point 6.2 was adopted for both January (I) and March (II). In March, the concentration of Cd at 6.2 (II) was below the limit of detection (< LOD), so for the background content of this element we used point 6.1 (II). Samples with index (I) were taken at the beginning of the austral summer and (II) at the end.

Sample n.o.	I_{geo} Cd [−]	I_{geo} Cr [−]	I_{geo} Co [−]	I_{geo} Ni [−]	I_{geo} Pb [−]
1.1 (I)	< LOD	−0.614	−0.008	−0.517	−0.124
2.1 (I)	< LOD	−1.558	−0.181	−1.210	−1.415
3.1 (I)	2.594	−0.504	0.080	−0.312	−1.273
4.1 (I)	1.090	−1.015	0.372	−0.625	−0.875
4.2 (I)	3.029	−0.189	0.523	−0.013	−0.215
4.3 (I)	3.988	−0.617	0.346	−0.235	−0.291
5.1 (I)	< LOD	−1.159	−0.426	−1.147	−0.423
1.1 (II)	1.638	−0.173	0.062	−0.325	1.643
2.1 (II)	< LOD	−1.711	−0.677	−1.677	−2.126
3.1 (II)	3.409	−0.217	0.432	−0.590	−0.031
4.1 (II)	−0.259	−0.987	−0.370	−0.832	−1.132
4.2 (II)	1.389	−0.308	0.156	−0.404	−0.922
4.3 (II)	1.684	−0.568	−0.051	−0.480	−0.486
5.1 (II)	−1.096	−0.792	−0.236	−0.994	−1.231

hydrothermal solutions could result in a higher content of Cu, Zn, Ga, Ba, B, and Li, and in Ca substitution by Na (Inoue, 1995). A higher content of Na than Ca and Mg may also be an effect of pyroclasts weathering (e.g. tuffs), if they contain more volcanic glass (Gifkins et al., 2005). In the rocks, the presence of secondary seladonite (a clay mineral from the mica group) was observed, which in these climate is rather a product of the impact of hydrothermal solutions on basalt rocks than the effect of their chemical weathering (Andrews, 1980). It should be noted that the abundance of organic matter in the samples from areas I and II may be related to the proximity of bog, characterized by rich vegetation of mosses. It may be an additional source of some metals (Pb, As, Cd), which this vegetation can accumulate, and which are rarely found in natural accumulations associated with basalt and andesite rocks (Birkenmajer, 2003). In addition, biological processes occurring in peat may be a source of TOC (Szopińska et al., 2018).

In the case of the sediment sample 2.1, the influence of seawater in the form of elevated SO_4^{2-}, Cl^-, F^-, Cl^-, Br^- is noticeable (eg. Horita et al., 2002). The presence of high concentrations of these ions results in a high value of conductivity in the sediment water extract. In sample 2.1, also the increased content of K^+ and Br^- and slightly elevated PO_4^{3-} was noted. These elements could come from the disintegration of primary minerals from this region, and can also be the result of the presence of marine algae in the sediment since they accumulate these elements (Birkenmajer et al., 1991; Birkenmajer, 2003). In this sample, there is also no very pronounced effect of hydrothermal solutions. The share of Li, Zn, Cu, Cs, Ba elements is already lower than in the sample 1.1.

The columnar jointing in the trachybasalt (or basalt) rocks is clearly visible in the area of Ornithologists Creek. There are also signs of secondary carbonate mineralization (calcite on trachybasalt). Typical contaminants for basalt and trachybasalt are found in the sediment sample 3.1. In addition to these, a relatively low pH is noticeable compared to other sediments, which may be the result of acidification with bird droppings. The TOC content in the sediment sample 3.1 was high in January, while in March it dropped. This is probably the result of washing out of the initial vegetation and bird droppings from the vicinity of the watercourse. This would be confirmed by the increased concentrations of PO_4^{3-} and NO_3^- (also higher values in January) (Szopińska et al., 2018). This indicates a significant advancement of the weathering processes, which is manifested by the increased content of Al (weathering basalt), but also Fe, Ni, Cr (Birkenmajer, 1996; Gifkins et al., 2005). Also noticeable is the increased content of Cd in January compared to March. Statistical analyses have shown that Cd correlates with the content of phosphorus, which comes from bird droppings (penguins, Antarctic skuas) and mammals (sea lions, sea elephants, leopard seal). In January, sediment 3.1 was characterized by high Na^+ content, which may be associated with the January supply of sodium from more distant parts of the area. In March, in turn, the Ca^{2+} content increased, which was a consequence of the concentration of calcium originating from the primary weathering rocks. The differences in the concentration of individual elements in these two months should not be associated with the binding of some ions in specific secondary minerals, because there is too short a time interval between them.

The sediment samples 4.1 and 4.2 were characterized by a similar sedimentation environment. The samples were taken from the bay sediments in the forefield of the Ecology Glacier. In the sediment sample 4.1, the chemical composition of the sediment was more clearly influenced by land, while in sample 4.2 the marine environment had a stronger impact. Both samples have high conductivity, typical for marine sediments. The samples show variability in the content of Cl^-, SO_4^{2-}, F^- and Br^-, which seems to depend on the local currents and tides within the bay, as well as the possibility of periodic water supply from the Admiralty Bay with freshwater from a melting glacier. The remaining minerals are typical for the weathering of parent rocks. A significant increase in the content of some metals may be related to their accumulation in marine algae and other sediment microorganisms from the Admiralty Bay.

The sediment sample 4.3 taken from the shore of small lake shows the content of elements typical for sediments from the weathering of the local geological substratum, in addition to the elements typical of the weathering of basaltoids, such as Fe, Ca, Ni, Co, Al (Gifkins et al., 2005). This may indicate more intense rock weathering processes around this measuring point, as well as the impact of past and current volcanic processes on this area among others from volcanic phenomena around Deception Island (Potapowicz et al., 2019).

A sample of sediment 5.1 was taken from the bay in the forefield of the Sphinx Glacier. In this area, the geological structure consists mainly of basalt rocks. However, the sediment composition was not typical for basalt weathering only. The higher alkalinity of the sediments, i.e. Na^+ and K^+ predominance over Mg^{2+} and Ca^{2+}, indicates the influence of sea water mineralization on the sediment. This is confirmed by the content of Cl^-, SO_4^{2-}, F^- (eg. Horita et al., 2002). In addition, elevated concentrations of NO_3^- in January may result from the flushing of bird and other animal droppings off the shore (Derry et al., 1999).

A sample of sediment 6.1 was taken from the bay adjacent to Baranowski Glacier. A significant share of alkali was noted in this sediment. The sample does not accurately reflect the composition of the sediment delivered from land. In comparison with sample 6.2, it contains much less Ca^{2+}, whereas more Na^+ and K^+. Sample 6.1 has a high pH value compared to other sediment samples. Conductivity is relatively low. Noticeable is also the disproportion of ion contents in January and March. Perhaps it is related to the more intense supply of meltwater with mineral matter in January and mixing it with the sediment accumulated earlier in the bay. The waters here seem well oxygenated, which promotes the activity of oxyphilic elements. In sediments, slightly lower impact of seawater is noted, as evidenced by the lower SO_4^{2-} and Cl^- content than in other samples. The presence of PO_4^{3-} ions in this sediment sample is probably related to the presence of bird and pinnipeds droppings.

A sample of sediment 6.2 was collected from the foreland of Baranowski Glacier in the place of sedimentation of both fluvioglacial and local fluvial material (in this location mainly tuffs and shale). The elevated concentrations of most elements in this sample are typical of alkaline and neutral volcanism. The presence of a large amount of Fe, Mn, Ca^{2+}, Al, Co, Ni, Cr, but also increased contents of Na^+, Rb, Li, Ba, and Ga, indicate a heterogeneous area. While the presence of the first group of elements is typical for the weathering of basaltic formations, the second group is probably more related to the weathering of soft volcanic tuffs, or shale, possibly additionally affected by hydrothermal metasomatosis (Gifkins et al., 2005). Increasing amounts of Rb, Ba, or Li

can be seen in the intensive weathering of mica and the presence of clay minerals that bind these elements (Deer et al., 2003). Very high Ca^{2+} content may have various causes, e.g. the concentration of this ion in clays, or the intensive weathering of calcium plagioclases, pyroxenes, hornblendes or zeolites. There is also a slight presence of NO_3^- and PO_4^{3-}, which is undoubtedly related to the presence of birds or other animals.

The drainage network created by water from melting glaciers has a high dynamics, which favors the enrichment of sediments in Fe and Al, thus also enriching the water flowing through the sediment (Brown, 2002; Tatur and Keck, 1990). Not without significance for the chemical composition of water samples is the rock weathering, which is the main natural factor shaping sediment chemistry. Several studies (Brown, 2002; Hodson et al., 2010; Szopińska et al., 2018) found that due to the prevalence of pyrite on the King George Island (Paulo and Rubinowski, 1987), there may occur the following reaction:

$$4FeS_2\,(s) + 14H_2O\,(l) + 15O_2\,(aq) \longleftrightarrow 16H\,(aq) + 8SO_4^{2-}\,(aq) + 4Fe(OH)_3\,(s). \quad (1)$$

In the water samples 3.1, 6.1, 6.2, it is possible to clearly observe the higher concentrations of TOC in January than in March. This may be due to the effect called "a spring pulse", which consists in the fact that during the winter precipitation components (ions, metals, organic matter) are stored in the snow cover, and then, during the spring thaw, these chemical entities are released into Antarctic waters (Waldner and Burch, 1996; Szopińska et al., 2016). A particularly strong "spring pulse" was observed in the sample 3.1 taken from the Ornithological Creek. Most likely, this is due to the fact that in the lower section of this watercourse we can find ornithogenic soils (Nędzarek et al., 2014). Additionally, this effect was observed in the water samples taken from the Baranowski Glacier (6.1, 6.2), which is probably related to the high intensity and melting rate of this glacier (Szilo and Bialik, 2017) and the release of sediments. Szopińska et al. (2018) also observed the same effect for areas II and VI. The lack of this effect in other water samples may result from a small amount of stored elements, chemical compounds, organic matter in the snow cover, as well as small amounts of sediment carried by the creeks.

The correlations between TOC and individual metals and non-metals, separately, are presented for water samples (Table 4A). No significant correlation was observed between TOC and other elements. Statistical analysis was illustrated by very strong correlations ($0.8 < |r| \leq 1$) between Fe and Al (0.915), Al and Zn (0.836), Fe with Cu, Ga. In addition, Li and B were very strongly correlated with a large number of elements (Li with: B, Ga, Rb, Sr, Cd, Cs, Ba, Pb and B with: Ga, Rb, Sr, Cd, Cs, Ba). Such correlations indicate that these elements may be of natural origin (Groeneweg and Beurik, 1992). It was shown that the content of Al_2O_3 and Fe_2O_3 in the rocks taken from King George Island were in the ranges of 18.41–21.72% and 8.16–9.48% respectively (Mozer et al., 2015). Thus, the correlation between Al and Fe confirms the links in the occurrence of these elements side by side. It was found that the presence of boron in the environment is mainly associated with volcanic activity, and B is a volatile element (Katalin et al., 2007). It has been proven that the occurrence of Zn, Cu, Mn and Co on King George Island, apart from anthropogenic sources, results from the chemical denudation processes during which water is enriched in these elements (Szopińska et al., 2018).

4.2. The influence of near and long-range anthropogenic activity on water and sediment chemistry

As mentioned in the previous subsection, sea aerosol has a major impact on the chemistry of waters and sediments in this area (Nędzarek et al., 2015). The SO_4^{2-} is present in both water and sediment samples, which results from the fact that the majority of water samples were taken from the Admiralty Bay. In addition, after the deposition, the sea aerosol has a greater impact on changing the chemical composition of waters than sediments due to the greater availability and rate of penetration of compounds in the entire volume of the matrix. It was proved that the sources of SO_4^{2-} ions in atmospheric transport should also be seen as anthropogenic (Budhavant et al., 2015; Giordano et al., 2016) and biological (Giordano et al., 2016). Graf et al. (2010) developed models of SO_2 distribution in Antarctica. The authors have observed that, apart from natural sources (volcanic processes), a huge influence on the concentration of this oxide comes from power generation and vehicle operation at and between stations, as well as from ship emissions. Graf et al. (2010) showed also that weather conditions in the area of Antarctic Peninsula, where further research bases are located, there is a reduction in the concentration of SO_2 because the oxidation to SO_4^{2-} is faster there due to higher temperatures, air humidity and insolation. Szopińska et al. (2018) showed that there is no significant difference in % nss SO_4^{2-} in freshwater from the western coast of the Admiralty Bay collected at the beginning and end of the austral summer. The authors said this may suggest a relatively regular influx of these ions throughout the austral summer.

The most common pollutants in the Antarctic area are those resulting from accidental fuel spills (Tin et al., 2009) and the use of petrol engines (Mishra et al., 2004). They are a source of toxic elements such as: arsenic, cadmium, copper, lead, mercury and zinc. It should be emphasised, that the sources of these heavy metals in the environment, besides human activity, are also natural, which is why it is important to distinguish the impact of these groups of factors. Due to the presence of many scientific stations and an increasing intensity of tourism in the vicinity of King George Island (Harcha, 2006), the anthropogenic impact on the chemistry of waters and sediments is inevitable (Szopińska et al., 2019).

Due to the spatial distribution of the sediment sampling points, the geoaccumulation index method was selected (Table 1). It allows to determine the anthropogenic impact on the environment pollution with heavy metals (Lu et al., 2012). The values of this index for Ni and Cr were below zero in all sediment samples in both January and March. This indicates that there is no contamination with these metals in the studied area. In the case of Pb, the majority of geoaccumulation index values were also negative, except for the 1.1 collected in March ($I_{geo} = 1.643$), from the lake in Jasnorzewski Gardens. According to the classification proposed by Müller (1981), this sediment is characterized by moderately strong lead pollution. However, due to the negative index for this sediment collected in January, it should be noted that at this point the pollution was not caused by human activity. It can be assumed that along with the spring thaws, Moss Creek began to wash sediments from the upper part of the watercourse containing lead compounds which were transported to the lake, where the concentration of lead increased compared to January.

The index values for Cu for sediments samples did not exceed 1 (6 of them were below zero), which means that there was no contamination with this metal. The highest levels of human impact involved Cd. It was determined that the points: 4.2 (I), 4.3 (I), 3.1 (II) were heavily contaminated with this metal. At points: 4.2 (I), 4.3 (I), 3.1 (II) there was heavy contamination, and at point 3.1 (I) moderate to heavy contamination. Possible anthropogenic sources of Cd are petroleum and wastewater disposal (Santos et al., 2005). This metal may also come from the release of pollutants stored in the permafrost (Potapowicz et al., 2019), but probably this source is less important.

4.3. Major factors shaping the chemistry in the coastal zone and the correlations between them: the PCA results analysis

The analysis of the chemical composition of water samples shows that it largely reflects the chemical composition of the sediments. Multivariate data set analysis enabled us to identify major trends in the chemical properties of the water and sediment in the study area. Both in January and March (Fig. 3), the waters on the western coast of

Admiralty Bay were distinguished by their Na^+, Cl^- and SO_4^{2-} concentration. These ions are clearly related to the impact of marine aerosols in the study area. In addition, anthropogenic and biological sources of SO_4^{2-} can be contributing through atmospheric transport (Giordano et al., 2016). The SO_2 may come from ship emissions, as well as stations, and become a secondary source of sulphates by oxidation of SO_2 to SO_4^{2-} (Graf et al., 2010). Both in January and March, it was observed that in the case of fresh water samples 1.1, 3.1, 4.3, 6.2, they show little affinity to ions coming mainly from sea aerosol (Na^+, Cl^-, SO_4^{2-}). Noteworthy are samples 2.1 (I and II) and 6.1 (I), because it has been shown that the sea spray has a slight effect on them, while these samples were taken from the bay. The reasons for this may be tides, glacier thawing and calving. However, we believe that these samples are a kind of anomaly and do not tend to shape water chemistry in these areas.

In contrast to the water data, for both series of sediments, two principal components were identified. The chemical variables that shape sediment chemistry in January were (Fig. 4A): (1) Na^+ and Fe, (2) Al and (3) Ca^{2+}. As far as Na^+ is concerned, it is undoubtedly from sea aerosol, whereas the presence of Fe, Al and Ca^{2+} is associated with the processes of chemical weathering of bedrock and surface sediments. For comparison, in March (Fig. 4B), the sediment chemistry was shaped similarly to January (1) Al, (2) Fe and additionally (3) P, which was not found among the chemical variables determining the shape of sediment chemistry in January. The sources of phosphorus in sediments are most probably penguin guano, resulting from the proximity of colonies of these birds in the studied area (Myrcha et al., 2013; Zwolicki et al., 2015). A particular affinity to total phosporus was found in sample 3.1 (II), which was taken from the Ornithologists Creek, characterized by a lush moss cover. The mosses could also affect the high total phosphorus content in the sediment sample.

Simas et al. (2007) proved that the ornithogenic influence affects the change of sediment properties. The effects of these changes are: soil acidification, leaching of exchangeable bases, transformation of minerals and release of metals like Fe and Al. The authors observed that the process of phosphating these metals occurs as a result of reaction with ornithogenic phosphorus. This has a direct effect on a predominantly phosphatic fine pool and a significant increase in sediment P pool, which is associated with rising levels of labile and moderately labile phosphorus. Thanks to this, P is temporarily detained in sediment in the form crystalline and non-crystalline Al/Fe phosphates, which are P reservoirs and are present in sediments even after penguins leave these areas. Higher levels of P content (along with N) in ornithogenic sediments favorably affect the growth of vegetation and make it more diverse (Smykla et al., 2011). It was also shown that many years after penguins abandon their colonies, the contribution of vegetation to chemical composition of the sediments is insignificant, but rich and biologically functioning microflora was found in the sediments (Smykla et al., 2015). In addition, a significant share of Fe in the costal environment of the Antarctic may come from the export of iron with surface runoff (Hodson et al., 2017). The runoff from headwater streams is mainly caused by climate warming (Hodson et al., 2017) and to a lesser extent by subglacial melting (Ardelan et al., 2010).

5. Conclusions

Antarctica is a unique laboratory for studying changes taking place in the world. This area is particularly sensitive to climate change, and as a result, an acceleration of the naturally occurring processes may be observed. This phenomenon can be also visible in geochemical analysis results. Based on the performed study, our main findings are as follows:

- As a result of physical weathering, the higher concentrations of Fe, Ni, Co, Al are noticeable.
- The effect of sediment acidification (higher phosphate concentration) in March is observed, that may also lead to exchangeable bases leaching, the transformation of minerals and an enhanced release of metals like Fe and Al.
- High concentrations of B and Sr compounds in the saline water may be caused by binding boron into the inter-package structure in illite. During diagenesis under the ocean floor, illite releases boron and then enriches water of the Admiralty Bay.
- As a result of anthropogenic activity, an increased content of Cd and Pb in the surroundings of the station is observed. Moreover, organic matter in this area may also be a source of these metals, since they may be accumulated by vegetation and they are rarely found in rocks of the basalt/andesite type.

Based on the assumption that the volume of Antarctic melt increases in response to observed climate change, the monitoring of the released elements needs particular concern, with a special focus on its seasonal dynamics and on pollution assessment.

Author contributions section

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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 for the manuscript "Seashore sediment and water chemistry at the Admiralty Bay (King George Island, Maritime Antarctica) – Geochemical analysis and correlations between the concentrations of chemical species"

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.110888.

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A continuation of the second hypothesis verification is presented in the paper: **Potapowicz J., Szopińska M., Szumińska D., Bialik R.J., Polkowska Ż., Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 1: Sediment and water analysis for PAH sources evaluation in the vicinity of Arctowski station, *Chemosphere*, 288 (2022) 132637 [publication V]**. The article presents research results that describe the chemical composition of PAH pollution in both sediments and water from the environment of King George Island and an assessment of the environmental fate of these pollutants, including the processes taking place in these two elements of the environment. The analyses concerned samples collected during the three years 2016–18 (two series each year – one each at the beginning and end of austral summer). The novel research results obtained from different matrices over three years allowed a determination of spatial distribution and defined which sources (pyrogenic or petrogenic) contribute more to PAH pollution in Antarctic sediments and water.

Based on the conducted research, it was found that sediments can be a reservoir of PAHs in the Antarctic environment. The sediment–water diffusion of PAHs was evaluated using the physicochemical partition coefficient for octanol–water (K_{OW}). It is typically assumed that PAHs adsorb to the organic fraction of samples, so total organic carbon (TOC) in water and in the sediment should be analysed for a full understanding of PAH partitioning. As a result of this analysis, it was found that the relationship of $\log K_{OW}$ to physicochemical partition coefficient for organic carbon ($\log K_{OC}$) can be concluded to be exponential. This proves that, at lower concentrations of organic carbon in Antarctic samples, the increase in PAH migration from sediment to water will be more intense than in urbanised areas.

Based on the conducted chemical analyses, it was observed that the concentration of PAHs in water changes seasonally, which is the result of the so-called “spring pulse” phenomenon caused during spring thaws by the release of pollutants accumulated in snow and firn. The origin of PAHs in the Antarctic environment was assessed using an analysis of PAH index values. It proved that pyrogenic or mixed sources contribute more than petrogenic sources to pollution by PAHs in Antarctic sediments and water. In addition, the main source is the combustion of biomass (e.g., as a result of fires) and coal that can

be assumed to be transported by LRAT from South America. Taking into account the indexes of petroleum-derived PAHs of naphthalene and its homologues, which are less stable than pyrene, fluoroanthene and other PAHs formed during fuel combustion, it was found that the dominance of pyrogenic sources is probably associated with the activity of the stations itself.

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Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 1: Sediment and water analysis for PAH sources evaluation in the vicinity of Arctowski station

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HIGHLIGHTS

- The concentration of PAHs in waters varies seasonally.
- The highest PAH concentrations in sediments were observed in 2018.
- Naphthalene, phenanthrene and anthracene are the dominant PAH congeners.
- Pyrogenic sources of PAHs dominate in the research area.

GRAPHICAL ABSTRACT

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ABSTRACT

The paper presents a study regarding the identification of polycyclic aromatic hydrocarbons (PAHs) in fresh waters and surface sediments on the western shore of Admiralty Bay over four sampling seasons from 2017 to 2018. The results were compared to literature data from 2016 to provide a more comprehensive image of the environmental fate of PAHs over the years. The highest value of Σ PAHs was 82.9 ng/L and 445 ng/g dw in water and sediment samples, respectively. The analysis of PAH indicator ratio values showed that pyrogenic or mixed sources contribute to the PAH pollution in Antarctic sediments and water more than does petroleum. The main source is the combustion of biomass (e.g. as a result of fires) and coal, and PAHs are mostly associated with the activity of stations or are transported to a lesser extent by long-range atmospheric transport (LRAT) from South America. The values of the ΣLMW/ΣHMW ratio in sediments indicate that petrogenic sources contribute to PAH contamination, but among the six PAH ratios tested, petrogenic sources were identified as dominant in approximately 17–19% of cases. Lack of coherence in the obtained results confirms the mixed origin of PAHs in the studied samples. Although the differentiation of PAHs sources is still ambiguous, caution is recommended in light of the Antarctic system's evident and rapid response to global and local PAH emissions, and the dependency

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of accumulation and release cycle processes on weather conditions. A reduction in petrol usage in favour of renewable energy sources, and restriction of tourism are strongly recommended for better preservation of the pristine Antarctic environment.

1. Introduction

Human impact on the Antarctic environment has been increasing over recent decades (Curtosi et al., 2009; Szopińska et al., 2019). A number of chemical pollutants, including persistent organic pollutants (POPs), have been proven to exist in Antarctica in both animate and inanimate elements of nature (Cipro et al., 2012; Curtosi et al., 2009; Martins et al., 2004; Potapowicz et al., 2019). One challenge faced by scientists, however, is that of compounds that, apart from having anthropogenic sources, may also be of natural origin, like polycyclic aromatic hydrocarbons (PAHs) (Cai et al., 2016; Cao et al., 2018; Cincinelli et al., 2008; Fuoco et al., 2012). The primary sources of PAH emissions are: incomplete combustion of biomass, fossil fuels, oil spills and diagenesis of organic matter (Cincinelli et al., 2008; Fuoco et al., 2005; Szopińska et al., 2019). PAH pollution in Antarctica reflects total pollution emitted in the Southern Hemisphere, in spite of the continent's comparatively (to the Northern Hemisphere) small land mass, low human activity, and short history of industrial activity (Cao et al., 2018). As a result of atmospheric circulation, dust transport and cyclic volatilisation/deposition processes (Cabrerizo et al., 2011), PAHs are distributed in various elements of the Antarctic environment, e.g. atmosphere (Cao et al., 2018), seawater (Fuoco et al., 2005), freshwater (Szopińska et al., 2019), sediments (Curtosi et al., 2007, 2009; Rodríguez et al., 2018; Sutilli et al., 2019) and biota (Curtosi et al., 2009). The various activities of numerous scientific stations also contribute to PAH pollution (Aislabie et al., 1999; Ferguson et al., 2003). Moreover, as a result of the increase in global temperature (Bockheim et al., 2013; Turner et al., 2016; Vaughan et al., 2003), a number of processes are affecting the chemical composition of different elements of the Antarctic environment. Glacier retreat (Pętlicki et al., 2017; Pudełko et al., 2018) and intensive weathering processes (Navas et al., 2017; Oliva et al., 2016a, 2016b) may cause the release of pollutants previously stored in ice (Herbert et al., 2006; Szopińska et al., 2018), permafrost (Potapowicz et al., 2019; Szopińska et al., 2019) and sediments (Martins et al., 2010; Pongpiachan et al., 2017; Potapowicz et al., 2020). Due to the multitude of sources of PAHs in the Antarctic environment, it was decided to determine it on the basis of PAH index values that were used in many previous studies eg. (Ravindra et al., 2008; Stogiannidis and Laane, 2015; Yu et al., 2015).

Considering the toxicity, mutagenicity and carcinogenicity of PAHs (Yang et al., 2014), and their tendency to bioaccumulate (Hale et al., 2008), exposure to PAHs in the Antarctic environment is a particular threat to the Antarctic fauna and flora (Lana et al., 2014; Mello et al., 2016). Most the study area belongs to Antarctic Specially Protected Area (ASPA) No. 128. This area is the place of breeding to three species of penguins (Adélie, Gentoo, Chinstrap), eight species of seabirds (e.g. southern giant petrel or south polar skua) and one representative of pinnipeds (i.e. southern elephant seal). PAHs have been observed to accumulate in mosses (Cabrerizo et al., 2012; Colabuono et al., 2015). The research may therefore be of key importance for the reduction of human activities potentially harmful to the Antarctic's pristine ecosystems. The primary objective of our research was (1) to present the chemical composition of PAH pollution in both sediments and water from the terrestrial environment of King George Island, and (2) to verify the accumulation and release cycle processes in sediment/aquatic environments over a three-year period (years: 2016–18). The novel research results obtained from different matrices over three years allowed us to estimate the mechanisms of PAH migration between various environmental media in the Maritime Antarctic. This study also includes a determination of spatial distribution and defines which sources (pyrogenic or petrogenic) contribute more to PAH pollution in Antarctic sediments and water. Considering the long-term character of the study, this paper may be a unique source of information on changes occurring in ASPA No. 128 and its surroundings. Furthermore, discussion of the results on the background of PAH levels in soils and waters at other sites may extend the knowledge about these contaminants and their accumulation in the Antarctic environment.

2. Materials and method

2.1. Site description and sample collection

The sampling area is located on King George Island (South Shetland Islands, Antarctic Peninsula). Water and sediment samples were collected from the largest ice-free areas on the western shore of Admiralty Bay (Fig. 1). Environmental factors potentially influencing the sampled water and soils were summarised (Table S1 [a–j]). Samples were collected twice during the austral summer of 2017 and 2018 (for details see Table S1). The first sample series (I) was collected in early summer, in January, when the snow cover was significantly reduced, while the second series (II) was collected in March or April, at the beginning of Antarctic autumn. Samples were taken from the forefield of the Ecology, Sphinx and Baranowski glaciers.

2.2. Analytical methods

Sixteen EPA PAHs in water and sediment samples were analysed. Samples preparation procedures are described in detail in the Supplementary Material. The PAHs were determined by gas chromatography tandem mass spectrometry using single ion monitoring mode. The system consists of an Agilent 7890B (Agilent Technologies, USA) equipped with a 7693A automatic sample feeder, and a 7000D GC/TQ triple quadrupole (Agilent Technologies, USA). The analyses were performed using Capillary GC Column Zebron™ ZB-PAH Capillary (30 m × 0.25 mm × 0.25 μm). The selected PAHs were determined based on the internal standard calibration method. The recovery (%) of individual elements and parameters was in a range 67–84% for water samples and 48–87% for sediment samples. Recoveries of surrogate standards were 81% and 83% for naphthalene-d8 and benzo(a)anthracene-d12, respectively. Blank sample analysis showed that the concentration of naphthalene in this sample was 0.11 ng/L, while the concentrations of the remaining PAHs were below the limit of detection. The limit of detection for each analyte was from 0.03 to 0.75 ng/L. Coefficient of variation (CV) was less than 5%. A detailed description of the monitored ions and detection limits can be found in Szopińska et al. (2019).

2.3. Statistical analysis

Concentrations of the target analytes that were below their limits of quantification (LOQs) were set to half the LOQ value for statistical purposes. A principal component analysis (PCA) was performed using MATLAB Version: R2020a with Statistics and Machine Learning Toolbox Version 11.7 manufactured by MathWorks, U.S.A.

2.4. PAHs diffusion between sediment: water phases

A useful source of information on the sediment–water diffusion of PAHs is the physicochemical partition coefficient for octanol–water (K_{OW}). It is typically assumed that PAHs adsorb to the organic fraction of samples, so total organic carbon (TOC) in water and in the sediment

should be analysed for a full understanding of PAH partitioning. The dependence of organic carbon (K_{OC}) to octanol–water (K_{OW}) partition coefficients for PAHs, and to the organic carbon fraction (φ_{OC}) of the sediment, is characterised by a linear relationship as follows:

$$\log K_{OC} = A \log K_{OW} + B$$

where A and B are values characteristic for individual PAHs. Furthermore:

$$K_{OC} = K_{SW} / \varphi_{OC}$$

where K_{SW} – sediment–water partition coefficient.

$$K_{SW} = C_S \rho_S / C_W$$

C_S – concentration in sediment, ρ_S – the density of sediment solids, C_W – concentration in water (Wang et al., 2011).

3. Results

3.1. PAHs in sediment samples

The chemical analyses of PAH contents provided results for sediment samples (Table S2). The last column shows total PAHs in each of the sediment samples in both measurement series. Concentrations of individual PAHs and their totals were much higher in sediments than in water samples. In 2017, total PAHs ranged from 58.8 to 383 ng/g dw in January, and from 58.4 to 389 ng/g dw in March. For comparison, these concentrations were 46.1–445 ng/g dw in January 2018 (series I) and 59.4–221 ng/g dw in March/April (series II). Differences in PAH concentrations depending on the year and series in which the sediment samples were taken are shown in Fig. 2.

It is worth noting that the highest concentrations of the total PAH in 2017 and 2018 compared to other sediment samples were found in samples B (264 ng/g) and D (445 ng/g) in January 2018 and in samples: A (389 ng/g) in March/April 2017 and B (383 ng/g) in January 2017. The lowest concentrations were found in sediment samples A in both series (I: 56.3 ng/g; II: 59.4 ng/g), C in January (46.1 ng/g) and E in both series (I: 68.5 ng/g; II: 62.9 ng/g) from 2018, and in samples C in both series (I: 58.8 ng/g; II: 58.4 ng/g) and E in January (68.4 ng/g) in 2017.

Both low molecular weight (LMW) and high molecular weight (HMW) PAHs were identified in almost all samples from both years. LMW PAHs include naphthalene, acenaphthene, anthracene, fluorene and phenanthrene. High-molecular-weight (HMW) PAHs, i.e., those with four or five rings, include fluoranthene, benzo(a)anthracene and chrysene. Naphthalene had the largest contribution in total PAHs in all samples, with the exception of sample B from 2017 taken from Ornithologists Creek (area II) in January. In this sample, phenanthrene had the largest share in PAHs. Benzo(a)anthracene showed lower concentration levels compared to other PAHs. Traces of five or six PAH rings were found in sediment samples from the western shore of Admiralty Bay at negligible levels or below detection limits.

3.2. PAHs in surface water samples

PAH concentrations in the studied surface water samples are presented in Table S3. PAH concentrations in water samples collected at the beginning of austral summer ranged from 0.53 to 32.4 ng/L, and at the

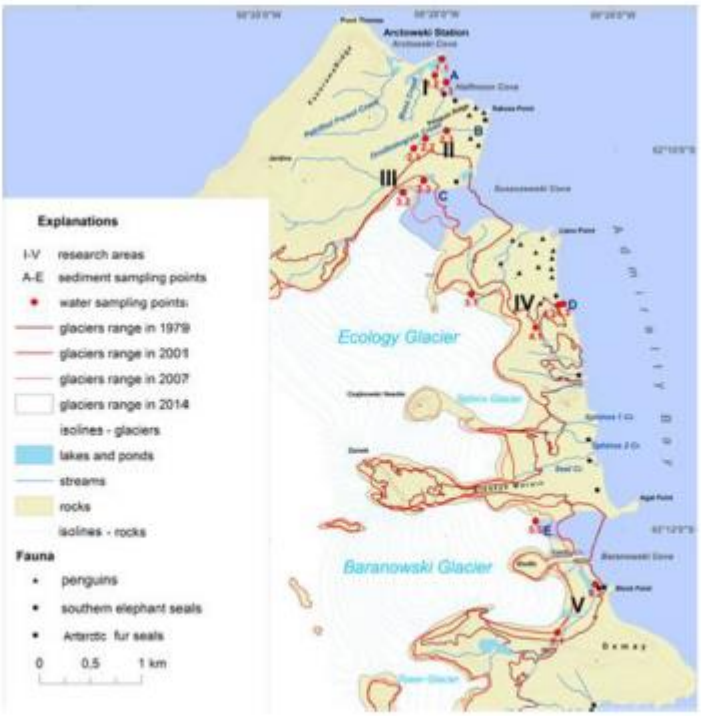

Fig. 1. Map of western shore of Admiralty Bay (Maritime Antarctica) showing glacier retreats between 1979 and 2014 and location of sampling points (prepared based on Pudełko, 2008; Landsat image LC82181032014016LGN00 obtained from www.usgs.gov; GoogleEarth application).

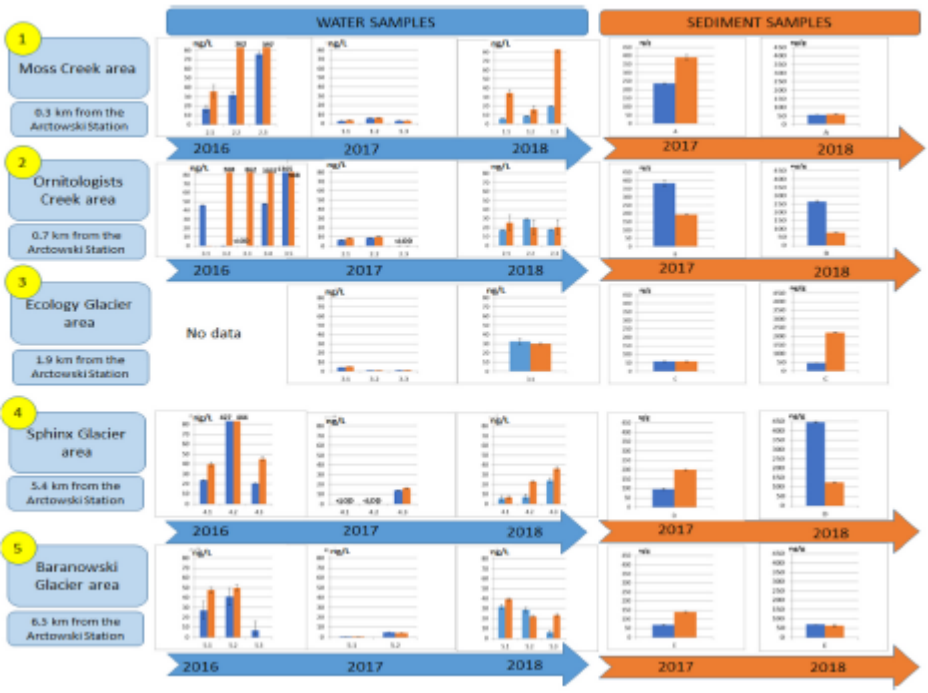

Fig. 2. Distribution of total PAHs in water and sediment samples during summer 2017 and 2018. Literature data for waters sampled in study area in 2016 taken from Szopińska et al. (2019). Values in blue and orange are derived from samples collected at the beginning and end of austral summer, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

end of austral summer from 0.58 to 82.9 ng/L, excluding samples: 2.3, 4.1, and 4.2 in which the concentrations of each PAH were below the limit of detection in 2017. In addition to the seasonal difference in concentration, variation was also apparent depending on the year in which the water samples were taken. The differences in PAH concentrations depending on year and sampling series are presented in Fig. 2. The ranges of ΣPAHs in 2017–18 were 0.53–15.8 ng/L and 5.38–82.9 ng/L for 2017 and 2018, respectively.

PAHs with two or three rings (LMW) have the highest contribution in total PAHs in both series. The presence of naphthalene was found in almost all water samples taken in both series, excluding samples: 2.3, 4.1, and 4.2 from 2017 (because of PAHs being below limit of detection at these points). Higher concentrations of acenaphthene, fluorene and phenanthrene were found in water samples from 2018. In 2017, the presence of these compounds was found in Moss Creek (area I), Ornithologists Creek (area II), and the forefield of Ecology Glacier (area III). In areas remote from the station (the forefields of Sphinx Glacier [area IV] and Baranowski Glacier [area V]), concentrations of these compounds were mostly below the limit of detection. In 2017, phenanthrene (0.40 ng/L in January and 0.42 ng/L in March) was found in sample 3.2, and fluorene (0.77 ng/L in January and 0.67 ng/L in March) and phenanthrene (0.98 ng/L in January and 0.65 ng/L in March) in sample 5.2. Anthracene was found in a small number of water samples. In the analysis of the sample from the middle section of Ornithologists Creek (2.2) from 2017, anthracene was found at a level of 1.10 ng/L in the first series (January), and 1.26 ng/L in the second series (March). In January 2018 (series I), significant anthracene concentrations were observed in the sample from the forefield of Ecology Glacier (3.1), and in March (series II) in the sample taken near Moss Creek (1.3).

Fluoranthene, one of the HMW PAHs was not identified in water samples from either of the years. Benzo(a)anthracene was only present in samples 4.3 (Sphinx Glacier area IV) from 2017 at 11.1 ng/L in January, and 13.1 ng/L in March, and in sample 1.3 (Moss Creek area I) from 2018 at 6.84 ng/L in March/April (series II). In sample 1.3 from 2018, in March/April (series II), the chrysene concentration was 5.53 ng/L, and in the remaining samples it was below the limit of detection. Five- and six-ring PAH concentrations were recorded as zero or negligible in water samples from the western shore of Admiralty Bay. It is not conclusive, however, that the compounds are absent in the studied area. The lack of HMW PAHs in water results from their low solubility in water and high affinity for organic matter.

3.3. *Multivariate data analysis result*

Principal Component Analysis was also conducted for all sediment and water samples. Some of the water datasets, however, were linearly dependent. Therefore, the results are not as expected and were omitted from further analyses. For sediment samples, two principal components were identified, representing 89% of the variance, and accounting for 58% and 31% of the variance, respectively (Fig. 3). The results showed a fairly strong positive correlation with naphthalene (0.60) and moderate positive correlation with anthracene (0.52) for PC1, and a fairly strong positive correlation with naphthalene (0.79) and moderate negative correlations with anthracene (−0.44) for PC2. The location of individual points representing the data provides an interesting image, and draws particular attention to data 1 (A form January 2017) and 16 (A from March 2018), which significantly affect the correlation with naphthalene. On the other hand, data 2 (B from January 2017), 3 (C from

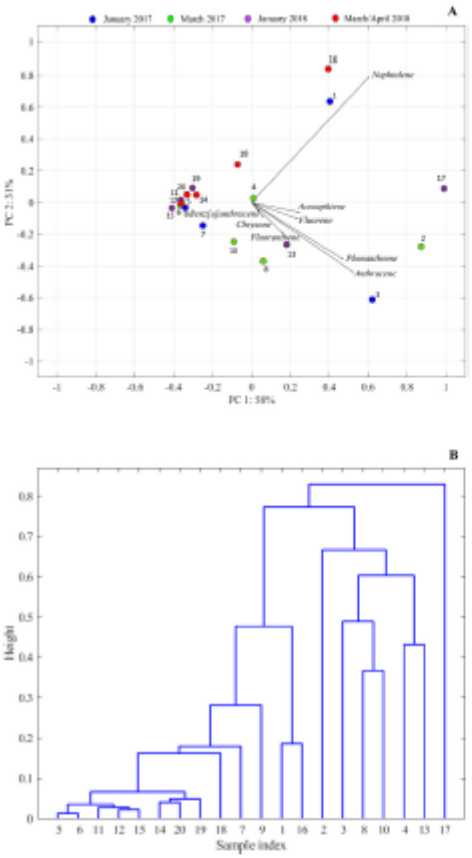

Fig. 3. PCA Biplots for various datasets (A) and dendrogram of sediments samples (B) taken in 2017 and 2018 from western shore of Admiralty Bay. Numbers 1–5 correspond to samples A–E from January 2017, respectively; 6–10 to A–E from March 2017; 11–15 to A–E of January 2018, and 16–20 to A–E of March 2018.

January 2017) and 17 (B from March 2018) generally result in a positive correlation of all variables.

3.4. Relationships between individual PAH concentrations and their sources in study area

PAH indicator ratios (Table 1) allow contamination sources to be identified. The six selected PAH ratios for individual environmental samples were determined based on descriptions included in other publications (Stogiannidis and Laane, 2015; Szopińska et al., 2019). The ratios allow results from 2017 to 2018 to be compared against results from 2016 (Szopińska et al., 2019). The identification of sources based on these results is ambiguous (in some cases different indices show different sources).

The PAH ratios: NP/PHE, BaA/CHr, PHE/ANT, ANT/(ANT + PHE) and BaA/(BaA + CHr) show a predominance of pyrogenic sources. Based on the calculation of the proportion between individual sample ratios indicating pyrogenic or petrogenic sources, it was found that pyrogenic sources dominated in all areas, being identified as dominating in 81.3–83.3% of cases (Fig. S3A). Petrogenic sources accounted for 16.7–18.8% of cases in areas I–V. In almost all of areas I–V, the NP/PHE values for both water and sediments were > 1. Exceptions were area II in January/February 2017, where the source of PAHs in surface waters was identified as pyrogenic, while PAHs in sediments were indicated as petrogenic; and the area IV in March 2017, where PAHs were of petrogenic origin, though this indicator could only be calculated for sediment. Moreover, the BaA/CHr analysis showed that the origin of PAHs is mainly pyrogenic, although the value of this indicator may only correspond to the state of sediments in the studied areas, because it was not possible to determine this value for waters (except for sample 1.3 in March/April 2018, indicating pyrogenic source). The ratio of (<1) ΣLMW to ΣHMW PAHs showed that, in surface waters in area IV, PAHs were also pyrogenic, while in sediments of the same area they were petrogenic. In other areas, both for water and sediments, the petrogenic source of PAHs predominated (based on ΣLMW/ΣHMW). All PHE/ANT values for sediment and water samples in 2017 and 2018 were <10, and ANT/(ANT + PHE) > 0.1, which indicates pyrogenic sources in all regions I–V. BaA/(BaA + CHr) values at all sampled points were >0.2, which also indicates pyrogenic sources of PAHs in the studied environment. The exception is point 4.3, where the ratio values in January/February and March 2017 were 0.01 (<0.2), indicating a petrogenic source.

The type of pyrogenic source of PAHs was also examined on the basis of BaA/(BaA + CHr) values for the sediments (Fig. S3B), with indicator values as listed in Guarino et al. (2019). This analysis showed biomass and coal combustion as the source of PAHs for almost all I–V areas in both measurement series of 2017 and 2018. An exception was area II in January/February 2017, with the pyrogenic source of PAHs identified as petroleum combustion.

Due to the different sources of PAHs in the Antarctic environment, the percentage contribution of 2, 3, 4 and more rings in PAHs was analysed (Fig. S3C). The share of 2-ring PAHs in sediments ranged from 29.8 to 83.3%, and in waters from 59.0 to 76.7%. The 3-ring PAH percentage was 14.8–59.0% for sediments, and 14.0–24.8% for waters. For areas I, II, IV and V, the percentage of 2-ring PAHs was higher in waters than in sediments. Similarly, the percentage of 4-and-more-ring PAHs in areas I, III, IV and V was also higher in waters. However, the share of 4-ring PAHs was generally similar in water and sediment, spanning 7.77–24.2% in water and 2.92–27.4% in sediment samples (for areas I–V). On the other hand, 3-ring PAHs were typically more abundant in sediment (at all locations except area III).

4. Discussion

4.1. Differences in PAH concentrations (sediments and fresh water)

Values of total PAHs in the sediments and water obtained in this study were approximate to those reported by past determinations of PAH concentrations for Antarctic sites (Table S4). For example, Cripps (1992) reported values ranging between 14 and 280 ng/g dw for the Signy Island, and Dauner et al. (2015) found 12.05–210.02 ng/g dw of PAHs in sediments from the vicinity of Carlini Station. Moreover, the sediments included more polluted ones, e.g. in a range of 36.5–1908.4 ng/g in the vicinity of Carlini Station (Curtosi et al., 2009), or 21.5–751 ng/g near Artigas Station (Rodríguez et al., 2018).

Σ_{16}PAH concentrations in the sediments in 2017 and 2018 examined in this study ranged from 56.3 to 445 ng/g. The exceptions are single measurement points near the research station, although constant pollution cannot be confirmed, because high values did not persist in more than one series of measurements for a given point.

PAH concentrations in water obtained in this study were lower than those obtained in sediments, and ranged from 0.53 to 82.9 ng/L. These values are approximate to those obtained by research conducted in Maritime Antarctica (Bícego et al., 1996; Cao et al., 2018). Compared to water samples taken in this area in 2016 (Szopińska et al., 2019), the

Table 1
Values of PAH indicator ratios for analysed sediment and water samples taken from western shore of Admiralty Bay during austral summer 2017 and 2018, and potential sources of emission of these compounds.

Year	2017						2018					
PAH indicator ratio[a]	NP/PHE	BaA/CHr	ΣLMW/ΣHMW	PHE/ANT	ANT/(ANT + PHE)	BaA/(BaA + CHr)	NP/PHE	BaA/CHr	ΣLMW/ ΣHMW	PHE/ANT	ANT/(ANT + PHE)	BaA/(BaA + CHr)
Sampling area												
1.1	–	–	–	0.78	0.56	0.36	41.14	–	–	0.78–1.00	0.50–0.56	0.36
1.2	7.45–10.21	–	–	0.98–0.99	0.50–0.51	0.36	24.92	–	–	0.78–1.11	0.47–0.56	0.36
1.3	2.07–2.26	–	–	0.99–1.01	0.50	0.36	33.27–33.4	1.24	5.7	0.94–0.96	0.51–0.52	0.36–0.45
A	1.2–8.97	1.36–1.42	10.8–18.04	0.98	0.50	0.58–0.59	17.14–30.61	0.75–1.13	27–133.05	0.98–0.99	0.50–0.51	0.43–0.53
Area I/source	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
2.1	3.59–4.35	–	–	0.98–0.99	0.50–0.51	0.36	32.86–41.93	–	–	0.95–0.98	0.51	0.36
2.2	1.33–1.34	–	–	0.99–1.01	0.50	0.36	12.84–27.16	–	–	0.99–1.04	0.49–0.50	0.36
2.3	–	–	–	0.78	0.56	0.36	25.47–41.96	–	–	0.98–1.00	0.50–0.51	0.36
B	0.88*-4.25	0.52–0.96	2.13–3.06	0.71–0.99	0.50–0.59	0.34–0.49	1.46–11.88	0.94–1.41	1.85–28.21	0.98–1.09	0.48–0.50	0.48–0.58
Area II/source	Pyrogenic/ *petrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
3.1	2.85–3.26	–	–	0.98–1.01	0.50	0.36	12.86–16.46	–	–	1.03	0.49	0.36
3.2	1.18–1.18	–	–	0.59–0.63	0.61–0.63	0.36	–	–	–	–	–	–
3.3	–	–	–	0.78	0.56	0.36	–	–	–	–	–	–
C	16.81–17.11	0.71–0.83	77.45–82.41	0.95	0.51	0.42–0.46	20.93–34.18	0.63	35.56–327.93	0.99–1.01	0.50	0.38–0.41
Area III/source	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
4.1	–	–	–	0.78	0.56	0.36	7.1	–	–	0.78–0.98	0.50–0.56	0.36
4.2	–	–	–	0.78	0.56	0.36	6.97	–	–	0.78–1.03	0.49–0.56	0.36
4.3	–	–	0.21–0.24	0.78	0.56	0.01**	28.88–33.79	–	–	0.90–0.92	0.52–0.53	0.36
D	0.95*-2.62	0.63	8.73*-43.42*	0.98–1.00	0.50	0.36–0.39	2.1–9.96	0.64–1.39	26.89–36.08	0.96–0.98	0.50–0.51	0.39–0.58
Area IV/source	Pyrogenic/ *petrogenic	Pyrogenic	Pyrogenic/ *petrogenic	Pyrogenic	Pyrogenic	Pyrogenic/ **petrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
5.1	–	–	–	0.78	0.56	0.36	16.71–36.9	–	–	0.98–1.02	0.50	0.36
5.2	3.29–4.57	–	–	0.98–1.26	0.44–0.50	0.36	12.94–62	–	157.89	0.52–1.02	0.50–0.66	0.36–0.46
5.3	–	–	–	–	–	–	10.24–25	–	–	0.98	0.51	0.36
E	1.35–9.03	0.62–0.83	14.79–25.08	0.98–1.03	0.49–0.50	0.38–0.45	31.48–34.22	0.65	78.67–232.07	0.95–0.98	0.50–0.51	0.39–0.56
Area V/source	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
Source												
Pyrogenic (combustion)	>1[b]	>0.5–1[c]	<1[d]	<10[e]	>0.1[f]	>0.2[g]	>1[b]	>0.5–1[c]	<1[d]	<10[e]	>0.1[f]	>0.2[g]
Petrogenic	<1[b]	<0.25–0.5[c]	>1[d]	>10[e]	<0.1[f]	<0.2[g]	<1[b]	<0.25–0.5[c]	>1[d]	>10[e]	<0.1[f]	<0.2[g]

[a] ΣLMW, sum of low molecular weight PAHs (two- and three-ring PAHs); ΣHMW, sum of high molecular weight PAHs (four- and five-ring PAHs); NP, naphthalene; PHE, phenanthrene; BaA, benzo(a)pyrene; CHr, chrysene.
[b] (Ravindra et al., 2008).
[c] (Stogiannidis and Laane, 2015).
[d] (Zhang et al., 2008).
[e] (Budzinski et al., 1997).
[f] (Tsapakis et al., 2003).
[g] (Yunker et al., 2002).

range of concentrations was clearly lower recorded in 2017 and 2018.

As presented in Fig. 3, the PCA performed for sediments in all series over two years showed that naphthalene represents the greatest contribution in chemical composition across the study area. Moreover, PC1 (58% of the variance) shows a strong positive correlation with naphthalene, phenanthrene and anthracene, and PC2 (31% of the variance) shows a strong positive correlation with naphthalene, and strong negative correlation with phenanthrene and anthracene. The dominance of NP, PHE and ANT in sediment samples may result from the fact they are characterised by relatively low molecular weight, high volatility and high solubility in water compared to other PAHs.

The analysis results suggest that the concentration of PAHs in various elements of the Antarctic environment depends on the nature and type of matrix. Based on Tables S2 and S3 (Supp. Mat.), it can be concluded that total PAH concentrations in sediments were multiple times higher than the concentrations of these chemical compounds in surface waters.

Fig. 2 shows total PAH concentrations in the studied years and seasons. In most cases, both in waters and sediments, total PAH concentration increased in March/April. Decreases have been observed in waters of Ornithologists Creek (point 2.2) in 2018, and similarly in soil sampled from the mouth section of this creek. The basin's surface at the middle section of Ornithologists Creek is characterised by patches of moss and lichens and initial humus level in the upper part of soil profiles. Moreover, the valley bottom is covered by muddy sediments accumulated in small, temporary reservoirs. This condition may support the accumulation of PAHs on sediment particles, but also the biodegradation of these chemicals by bacteria is possible (Curtosi et al., 2007; Kosek et al., 2018). In March/April, the other streams carry greater PAH loads than in January – through rainfall and washing out the fine particles (clay and mud) into streams.

The affinity of individual PAHs to sediments or water samples depends strongly on the $\log K_{OW}$ value (Table S4). Considering PAHs, the applied K_{OW} is approximately equal to K_{OC} because exponent A approaches a value of 1 (Wang et al., 2011). As a result, the concentrations of PAHs should be proportionally higher in the sediments than in the water samples. However, it should be noted that the parameter of organic carbon that applies to samples in the vicinity of the Polish Antarctic Station (samples 1.3, 4.4, A and D) was determined in water and in the aqueous extract for sediments. Based on the data in Table S4, it can be concluded that the sediments are a larger reservoir of PAHs than are water. The relationship of $\log K_{OW}$ to $\log K_{OC}$ (formula in section 2.4) shows that K_{OW} and K_{OC} are linked by an exponential relationship. Thus, at lower concentrations of organic carbon in Antarctic samples, the increase in PAH migration from sediment to water will be greater than for, for example, samples from China (Wang et al., 2011). The low and medium molecular weight PAHs may change their transfer tendency between sediment and water (Wang et al., 2011), but in our samples the sediment concentration was always higher than the equilibrium value.

Rapid drainage of porous soils related to rainfall and snow- and ice-melt during summer could be the cause of a considerable inter-annual change in PAH concentrations in soils (Curtosi et al., 2007). This is called the 'spring pulse' phenomenon, caused by the release of pollutants accumulated in snow and firn during spring thaws. It primarily occurred in the early summer of 2017 and 2018 in the Ornithologists Creek area. It was also observed in 2018 in the Sphinx Glacier area (for sediment). The presented data show that in the case of creeks with non-glaciated catchments (I and II), where flowing waters are fed by rain, snow-melt, buried-ice-melt, and shallow groundwater in the active layer, levels of PAHs in water and sediment samples were different than those for creeks with a glacier-melt source of water (areas III–V) (Fig. 3). Other differences between catchments I and II and catchments III–V include the occurrence of mosses and lichens that support accumulation of PAHs in the hummus soil horizons (Gabov and Beznosikov, 2014). This vegetation type and soil type occur in areas I and II.

4.2. Sources of PAHs in environmental samples from Maritime Antarctica

Pyrogenic and petrogenic sources were identified based on PAH ratios (Table 1). The results of PAH ratios we obtained clearly indicate the domination of pyrogenic sources (Table 1, Fig. S3A). Moreover, based on the BaA/(BaA + CHr) values in sediments (Fig. S3B), it was found that PAHs in the research area mainly come from the combustion of biomass and coal. Since the nearby research stations do not use such fuel, we interpret that the primary source of PAHs on the western shore of Admiralty Bay is long range atmospheric transport (LRAT), which involves both pyrogenic and petrogenic sources. Such an interpretation is also confirmed by previous studies (Lammel et al., 2015) discussing the relationship of PHE and NP concentrations with LRAT.

The analysis of back trajectories incoming into the South Shetland Islands provided in previous research (Fernandoy et al., 2018; Szumińska et al., 2018) and in Szumińska et al. (2021) Part 2 (submitted) show the possibility that air masses incoming to the South Shetland Islands originated over inhabited regions (mostly South America). The frequency of air masses incoming from this area are in the range of 1–10% for the period of September 2016 to February 2017 and 5-day trajectories (Szumińska et al., 2021) (Part 2, submitted).

Additionally, our research confirmed the dominant share in the supply of PAHs from biomass and coal combustion (Fig. S3B). Due to LRAT, PAHs may also be transferred as a result of biomass combustion products, including those originating from fires, e.g., forest fires, bush fires and urban areas. Pollutants delivered to Antarctica this way are subject to dry and wet deposition in various elements of the environment (Curtosi et al., 2007; Fuoco et al., 2012; Szopińska et al., 2019). In 2018, compared to 2017, there was a clear increase in the total PAHs in waters (Fig. 2). As mentioned earlier, our results indicate that biomass combustion is the main source of these chemicals in the research area (Fig. S3B). In addition, the National Institute for Space Research (Inpe) reported, based on satellite imagery data, that there was an 84% increase in the number of fires in Brazil in 2018 (Andreoni and Hauser, 2019; BBC, 2019), which may plausibly explain the increased PAH concentrations from LRAT.

Despite human activity, South America also has numerous active volcanoes. The most active volcano in South America is Villarica in central Chile. It has been recorded to have been active for a total of 142 years between 1558 and 2017 (Szumińska et al., 2018). A total of six volcanoes were identified to be active in 2016 and 2017: Villarica, Láscar, Nevados de Chillán and Copahue in Chile, and Sabancaya and Ubinas in Peru (Fig. S1). In the next year – 2018 – most were still active (except Láscar and Ubinas) (www.volcano.si.edu).

Taking into consideration air masses frequency analysed by Szumińska et al. (2018), it is worth emphasising that the highest number of days with air masses incoming from South America together with high volcanic activity in the winter months of 2017 (May–Aug, Fig. S1C), and potential storage of PAHs in snow and ice may have contributed to its high levels in waters in the following spring–summer season (Fig. 2).

In areas I, II, III and V, in both water and sediment samples, the ΣLMW/ΣHMW ratio indicated the petrogenic source of PAHs as dominant. This demonstrates the potential contribution of direct petrogenic sources (such as diesel oil spills, particularly near station facilities). They are a minority compared to pyrogenic sources but should not be underestimated (Fig. S3A), as in this environment (the western shore of Admiralty Bay) they are closely related to the activity of scientists, as well as the maintenance and logistics of research stations. Considering that there are a total of 20 scientific stations (year-round and temporary) in South Shetland Islands (Bartolini et al., 2014), the load of chemical pollutants, including PAHs, they emit to Antarctic waters and sediments can be assumed to be significant. As our research has shown, in comparison with the percentage of pyrogenic sources, the activity of research stations located on Admiralty Bay does not have a major impact on the pollution of PAHs on the western shore of Admiralty Bay.

5. Conclusions

Research studies on the evaluation of PAHs are special important to protect the Antarctic environment against unforeseen anthropogenic activity. Based on our results, the main assumptions are as follows:

- It can be concluded that sediments can be a reservoir of PAHs in the Antarctic environment. The relationship of $\log K_{OW}$ to $\log K_{OC}$ can be concluded to be exponential, which proves that at lower concentrations of organic carbon in Antarctic samples, the increase in PAH migration from sediment to water will be more intense than in urbanised areas. The maximum value obtained for water was 82.9 ng/L, and for sediments 446 ng/g dw for ΣPAHs.
- The content of PAHs in water changes seasonally and between the two years, and in 2017–18 it was in the range 0.53–82.9 ng/L, which is the result of the 'spring pulse' phenomenon caused during spring thaws by the release of pollutants accumulated in snow and firn.
- Based on the analysis of PAH index values, it was determined that pyrogenic or mixed sources contribute more than petrogenic sources to pollution by PAHs in Antarctic sediments and water. In addition, the main source is the combustion of biomass (e.g., as a result of fires) and coal that can be assumed to be transported by LRAT from areas of South America. However, considering that the indicators of petroleum-derived PAH genesis are naphthalene and its homologues (which are less stable than pyrene, fluoroanthene and other PAHs formed during fuel combustion), the dominance of pyrogenic sources is probably associated with the activity of the stations itself.

In addition, the obtained results also confirm observations made in our previous studies:

- In contrast to Szopińska et al. (2019) a decrease in the value of ΣPAHs in water compared to 2016 was observed. In addition, comparing PAH concentrations in waters in 2018, their level increased compared to 2017, which may be due to the 85% increase in fires in Brazil.
- As part of the research presented in this article (samples taken in 2017 and 2018) and previous research by our team (Szopińska et al., 2019) (samples taken in 2016), a trend of higher levels of ΣPAH concentrations in the area surrounding the research station was observed. Therefore, incidental oil spills while using diesel fuel cannot be ruled out as a source of organic pollutants, including PAHs, in this environment.

Detailed PAH analyses in precipitation, snow cover, vegetation and animal tissues should be carried out in the future to provide a complete image of their environmental fate in Antarctica. Precipitation analyses in particular could help identify more precisely the sources of PAH pollution. Our results also call for petrol usage to be reduced in favour of renewable energy sources, and for tourism to be restricted for better preservation of the pristine Antarctic environment.

Credit author statement

Joanna Potapowicz: Conceptualization, MethodologySoftware, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration. Danuta Szumińska: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Project administration. Małgorzata Szopińska: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration. Robert Józef Bialik: Conceptualization, Software, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization. Żaneta Polkowska: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

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

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An additional threat to the Antarctic environment is the re-release of pollutants from snow cover under appropriate conditions. Re-emission into the environment of volatile and semi-volatile compounds during austral summer, and surface runoff of organic and inorganic composition (the so called "spring pulse"), cause snow to be considered as a secondary source of pollution. This effect was described and confirmed as part of the verification of the previous research hypothesis, which inspired more detailed research on this topic. Detailed results are presented in the article below.

In the publication VI: **Szumińska D., Potapowicz J., Szopińska M., Czapiewski S., Falk U., Frankowski M., Polkowska Ż., Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 2: Organic and inorganic chemicals in snow cover at the Warszawa Icefield, *Sci. Total Environ.*, 796 (2021) 149054** is presented the verification of the second detailed hypothesis too. The article presents the chemical characteristics of snow cover on King George Island. In addition, an analysis of the effects of the activity of polar stations and long-range atmospheric transport of chemicals was carried out. Surface snow samples were collected in the summer season of 2017 in a transect crossing the Warszawa Icefield area. The transect was located in the main ice cap between the Arctowski Polish Antarctic station and Carlini Base (Argentina) and in Ecology Glacier. Selected chemical species, including those classified as pollutants, were determined in the samples. Snow from the western coast of Admiralty Bay was analysed for concentrations of elements (Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, V, and Zn), cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}), anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), total organic carbon (TOC) and polycyclic aromatic hydrocarbons (PAHs).

The results obtained at the Warszawa Icefield confirmed the occurrence of chemicals (including contaminants) in snow cover. In addition, the results of determinations of chemical compounds and the analysis of the trajectory of air masses for the study area allowed us to state that the nearest scientific stations have only a limited influence and that the origin of the pollutants was mainly atmospheric (from regional and LRAT sources). A slight increase in ΣPAHs and trace metals was also observed at the marginal parts of the icefield, which may be caused by the influence of scientific stations

and more effective local dust at the edge of the glacier. Naphthalene and fluorene predominated across all the study sites except the one close to the Arctowski station, where phenanthrene was observed in snow. All three compounds are present in diesel, so their presence in snow samples may be related to the exploitation of fossil fuels. The local topography is an important factor in the deposition of aerosols at the dynamically changed ice-free areas of Maritime Antarctica, the consequence of which may be the potential negative effect for fauna and flora in this pristine area.

The verification of the hypothesis using analytical techniques and chemometric tools showed that:

- there are water–sediments–snow interactions that affect the chemistry of each of the three matrices;
- the relationships between the studied elements of the environment favour the distribution of chemical species, including pollutants, on the west coast of Admiralty Bay;
- no clear effect of the "spring pulse" was observed, but the presence of contaminants in snow presents a risk of their transfer to other components of the environment (including sediment and water) during the temperature increase.

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Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 2: Organic and inorganic chemicals in snow cover at the Warszawa Icefield

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HIGHLIGHTS

- Anthropogenic impact on Antarctic snow pollution (organic & inorganic) was observed.
- Concentration of elements <30 mg/L, TOC <1 mg/L and PAHs 0.11–1.4 ng/L in snow
- A greater diversity in marine-origin ions was found than in previous research.
- Dominance of naphthalene and fluorene was observed in all samples.

GRAPHICAL ABSTRACT

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ABSTRACT

The study area is located on King George Island, where 90% of the area is permanently glaciated. This study provides a comprehensive analysis of the inorganic and organic chemistry of snow cover in the icefield and a comparison against previous results obtained in fresh water. Snow samples were collected in the summer of 2017 in the Warszawa Icefield area. Sampling points are located along two transects: between the Arctowski Polish Polar Station and the Carlini Base (N = 4), and from the forefield to the upper part of Ecology Glacier (N = 5). In the snow samples, (1) basic ions, (2) major trace metals and metalloids (and B), and (3) polycyclic aromatic hydrocarbons (PAHs) were detected and quantified. Additionally, the parameters of pH, specific electrolytic conductivity (SEC_{25}) and total organic carbon (TOC) were determined. The results show a low concentration of inorganic elements (<30 mg/L), TOC (<1 mg/L) and PAHs (0.11–1.4 ng/L) in collected snow samples. A slight increase in PAHs and heavy-metals concentration has been observed at the marginal parts of the icefield, which suggests the impact of scientific stations. Based on this result there is a need to conduct research on pollutant levels in ice cores on King George Island to assess the risk associated with rapid glacier thawing and pollution remobilisation.

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1. Introduction

Antarctica is undeniably the continent least modified by anthropogenic activity.

Nevertheless, since 1969 (Peterle, 1969) signs of global pollution (pesticide – dichlorodiphenyltrichloroethane, DDT) have been noted at detectable levels in snow.

The cryosphere encompasses all surfaces that contain water in solid form, as snow and ice surfaces, which cover approximately 98% of the Antarctic continent (Kang et al., 2012). Furthermore, phenomena observed in snow cover or ice may indirectly reflect the actual state of the atmosphere. Analysing the properties and composition of snow, extreme atmospheric pollution may be visible (inter alia, Bargagli, 2005; Fuoco et al., 2012; McConnell et al., 2014) in chemical composition, as wet and dry deposition on it (Bargagli, 2005). Recent literature has reported a wide range of chemical characteristics of Antarctic snow. This includes both inorganic species: nitrates (Jiang et al., 2019) and other inorganic ions (Khodzher et al., 2020), dissolved iron (Liu et al., 2019) and heavy metals like mercury (Mão de Ferro et al., 2014; Pérez-Rodríguez et al., 2019); and organic species: organochlorine pesticides (Kang et al., 2012), per- and polyfluoroalkyl substances (Cai et al., 2012), polychlorinated dibenzo-p-dioxins and dibenzofurans, polychlorinated biphenyls and polybrominated diphenyl ethers (Fuoco et al., 2012; Vecchiato et al., 2015) and polycyclic aromatic hydrocarbons (PAHs) (Cao et al., 2018; Fuoco et al., 2012; Nemirovskaya, 2006; Vecchiato et al., 2015). Moreover, dissolved organic carbon in the form of acetate and formate (Samui et al., 2017), and organic traces from biomass burning – levoglucosan, vanillic and syringic acids (Shi et al., 2019) were also determined.

Special attention was also paid to the pollutant sources and transport mechanisms, as well as the environmental fate of pollutants in Antarctica (Bargagli, 2005; Potapowicz et al., 2019). Due to its nature, snow acts a transport medium for pollutants, which are flushed from the atmosphere and accumulate on the snow surface (Bargagli, 2005). Local and long-distance sources of pollutants described in various Antarctic environments include contaminants of both natural and anthropic origin (inter alia, Amaro et al., 2015; Bargagli, 2016, 2008, 2005; Kukucka et al., 2010; Padeiro et al., 2016; Pérez-Rodríguez et al., 2019). Some chemicals are strictly dependent on anthropogenic activity, e.g. organic volatile and semi-volatile compounds like pesticides and dioxins, which have been attributed to long-range atmospheric transport (LRAT) from the continents (Vecchiato et al., 2015; Wania et al., 1999) and the so called grasshopper effect – a series of evaporation, condensation/desorption. The others, like selected ions and trace elements, may originate from local natural sources, mainly rock weathering, aerosols, Antarctic biota activity (Szopińska et al., 2018) and hydrothermal processes in the active volcanic area (Mão de Ferro et al., 2013). However, some of them, such as mercury, due to its high volatility and long resistance time, may be transported/distributed over long distances from global atmospheric sources (Bargagli, 2016, 2008; Pérez-Rodríguez et al., 2019) and may also originate from local volcanic activity on Deception Island (Mão de Ferro et al., 2014). Likewise, with the species like nitrates and sulphates, as well as polycyclic aromatic hydrocarbon compounds, both local and long-range atmospheric transport needs to be considered. Moreover, anthropogenic and natural processes such as biomass burning, volcano eruption (PAHs, sulphates) and nitrate production from NOx (Dibb et al., 1998) in the atmosphere may be also taken into data interpretation.

Moreover, the processes occurring at the snow surface are important, too. Snow and firn metamorphism processes depend on temperature fluctuations. When grain growth occurs, this increases the firn permeability, and contaminants are transferred to the deeper layers. As a consequence, the accumulation of the various aforementioned groups of compounds in the cryosphere leads to them being trapped them in polar areas and creates long-term hazard conditions (Szopińska et al., 2017). Another phenomenon that may occur is re-release of pollutants to the environment under appropriate conditions. The re-volatilisation of volatile and semi-volatile compounds during the warmer months, and surface runoff of organic and inorganic composition (the so called '*spring pulse*') may cause snow to be considered as a secondary source of pollution (Szopińska et al., 2018, 2019).

Despite a growing interest in snow sample analysis in Antarctica (Bertler et al., 2005; Nemirovskaya, 2006; Vecchiato et al., 2015) there are still large knowledge gaps, and a comprehensive understanding of atmospheric pollution transport processes in biogeochemical cycles is still needed. However, there is no doubt that the atmosphere plays a crucial role in transporting any substances for local or long-range distances (Bargagli, 2016; Chambers et al., 2014; Mão de Ferro et al., 2014). In a polar environment, contaminants stored in snow may be released directly during seasonal thawing or stored for long times in glacial ice (Bertler et al., 2005; Fuoco et al., 2012; McConnell et al., 2014). Comprehensive analysis of inorganic and organic chemistry of snow cover may be useful in the ongoing discussion of the transport tracts of pollutants into and within the Antarctic environment, in particular pollutants of anthropogenic origin.

In this study, the snow samples were collected in the Warszawa Icefield (King George Island) in February 1st of 2017 (the early summer season). Sampling sites are located at different distances from the Polish and Argentinian polar stations, which are possible sources of pollutants. The studied Warszawa Icefield is a complex drainage system that consists of several land-terminating and tidewater glaciers. Ablation water and water from glacial drainage constitute one of the main sources of supply of water and contaminants for the fresh and marine waters at the western shore of Admiralty bay. Previous research conducted at the study area has pointed to the occurrence of organic pollutants in air (Cabrerizo et al., 2014), fresh and marine waters and sediments (Potapowicz et al., submitted, Part 1; Potapowicz et al., 2020; Szopińska et al., 2019), marine waters and sediments (Bícego et al., 1996; Martins et al., 2010), and Antarctic seabirds (Taniguchi et al., 2009). Therefore, this study tests the hypothesis of the possible occurrence of chemicals referred to as contaminants in snow cover on KGI. Moreover, the possible influence of polar stations' activity and long-range atmospheric transport of chemicals will be discussed. The conducted research, including sampling over a short period of time at sites of various distances from the scientific stations will allow it to be checked whether the stations are the local sources of inorganic pollutants. However, due to limited local sources of organic pollutants, that was selected for analysis (PAHs), the results may also be useful for answering the question of whether regional or long-range atmospheric transport (LRAT) is the pathway by which these contaminants are delivered.

2. Study area and sampling design

The study is located on the King George Island (KGI) (1310 km^2), which is the largest of the South Shetland Islands, where 90% of the area is covered by a polythermal ice cap (Falk et al., 2018) with a mean ice thickness of approximately 240 m (Rückamp and Blindow, 2012). Research was conducted in the Warszawa dome, which covers the area between the western shore of Admiralty Bay and Potter and Marian coves (Fig. 1). The complex drainage system of the ice cap is determined by the underlying geological structure (Braun and Hock, 2004) and includes two types of glaciers: land-terminating and tidewater glaciers. Glaciers at the western shore of Admiralty Bay and the unglaciated areas of its forefields belong to Antarctic Specially Protected Area 128 (ASPA No. 128), which was established in order to protect areas featuring important or unusual assemblages of species against unforeseen and potentially hazardous human activity.

The most visible environmental changes during the last half century in the study area are climate warming (inter alia, Bockheim et al., 2013; Kejna et al., 2013; Siegert et al., 2019; Turner et al., 2005) and related glacier retreat (Pętlicki et al., 2017; Pudełko et al., 2018; Sziło and

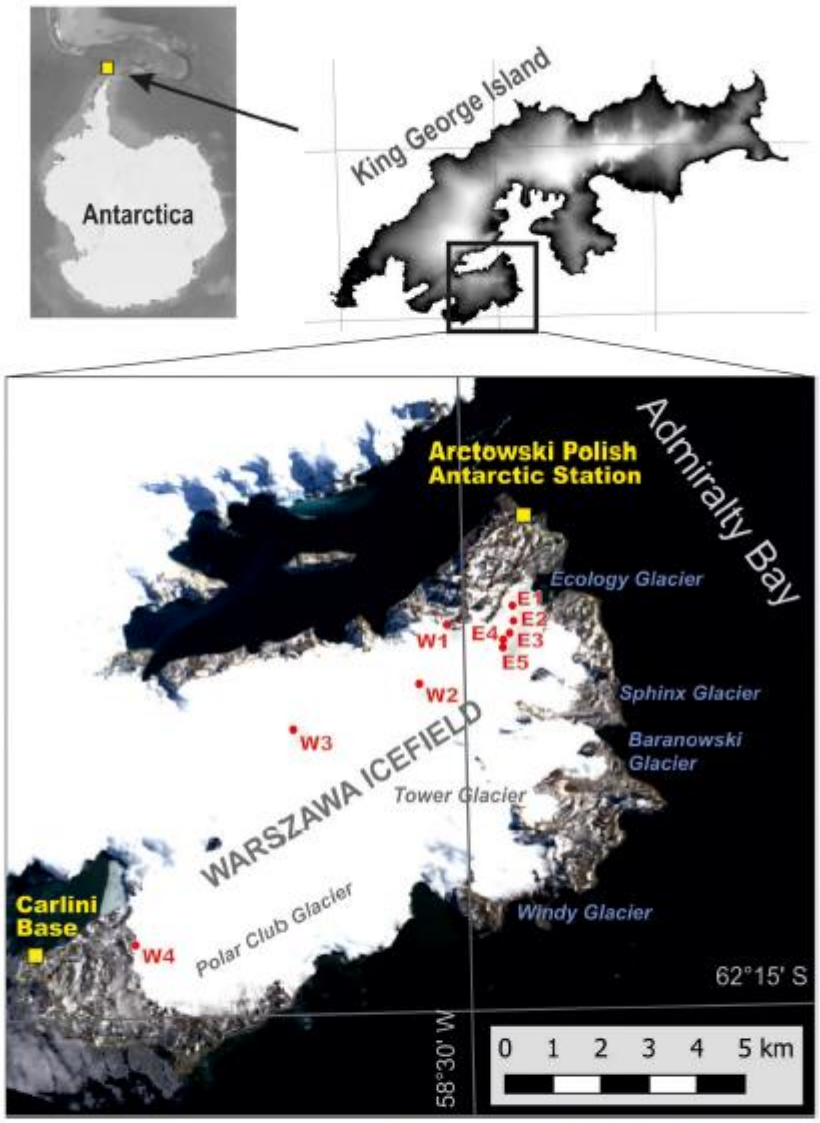


Fig. 1. Study area and sampling points location (prepared based on Landsat Image LC08_L1GT_217103_20180309_20180320_01_T2 – Level 2, obtained from www.usgs.gov, Google Earth application) (Google Earth, 2018; USGS.gov, 2018, p. 08).

Białik, 2018). According to Pudełko et al. (2018), ASPA 128 lost around 30% (6.1 km^2) of its glaciated area between 1979 and 2018. The process of deglaciation was the fastest in the periods 1989–2001 and 2007–2011. Detailed research shows that glaciers in the research area have been subject to strong negative mass balance since 1979, including lateral changes and also the vertical lowering of the ice surface (Pętlicki et al., 2017; Sziło and Białik, 2018) of the Baranowski Glacier. Between 1979 and 2016, the ice elevation of Ecology Glacier has constantly decreased, though the rate of lowering was not stable and amounted to -1.7 ± 0.4 m/year in 1979–2001, -1.5 ± 0.5 m/year in 2001–2012, and -0.5 ± 0.6 m/year in 2012–2016 (Pętlicki et al., 2017). A decrease in the ablation rate in the second decade of the 21st century was driven by regional cooling observed in the Antarctic Peninsula (Oliva et al., 2017).

In this study, surface snow samples (9) were collected in the summer season of 2017 in the transect crossing the Warszawa Icefield area (Fig. 1). The transect was located in the main ice cap between the Arctowski Polish Antarctic station and Carlini Base (Argentina)

(samples W1, W2, W3 and W4) and in Ecology Glacier (samples E1, E2, E3, E4 and E5). Moreover, one BLANK sample of deionised water was kept frozen from the date of sampling (2017, Feb 6th).

3. Laboratory and computed methods

The analysed snow cover samples were collected manually to polyethylene bottles (two 1-L samples from each point, in order to obtain approx. 1-L of liquid sample). All bottles were rinsed twice with deionised (DI) water and dried prior sampling. During sampling the air temperature was approximately −3 °C, there was a moderate wind speed of 5 m/s, and there was intense direct solar radiation. Samples collected at the Ecology Glacier (E1–E5) were taken during a walking route on the glacier. Samples from the Warszawa Icefield (W1–W4) were collected during snowmobile trips. Therefore, samples were taken at a distance of 50 m from the track. However, due to ASPA 128 protection rules, the use of snowmobiles in the Warszawa Icefield is sporadic. All samples were frozen and stored at −20 °C. To eliminate their possible contamination due to storage in a polyethylene container, one of the containers was filled with deionised water (blank sample) from the laboratory at Arctowski Station (Milli-Q system, Millipore GTTP, USA) and subjected to the same treatments as the environmental samples. After transporting to Poland, the samples were kept frozen, then thawed before the analyses. Snow samples were handled with special care to avoid cross-contamination.

During studies, advanced analytical techniques enabling the detection and determination of many analytes during a single measurement cycle were applied (Supp. data, Table S1). Concentrations of the 18 elements Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, V, and Zn were analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Major cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) and anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were determined using Ion Chromatography. PAHs were analysed using the internal standard calibration method, liquid–liquid extraction and gas chromatography tandem mass spectrometry. All details regarding the operational conditions of applied analytical techniques are available in Supp. data S1. Precision errors for the ions, all elements, TOC and PAHs analyses were 5% according to repeat analyses of mid-range standards.

The contribution of the non-sea-salt (nss) component of SO_4^{2-} was calculated using the equation: $nssSO_4^{2-} = SO_4^{2-} - (SO_4^{2-}/Cl^-)_{seawater} * Cl^-$. The $(SO_4^{2-}/Cl^-)_{seawater}$ ratio is the equivalent ratio of SO_4^{2-} to Cl^- in global mean seawater, which is 0.103 (Stumm and Morgan, 1996).

The origin of air masses was modelled with NOAA HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory, version 5) (Draxler et al., 2020; Stein et al., 2015). For calculations, the "Reanalysis" database was used, which in this case is the name of a dataset in the HYSPLIT services to calculate trajectories, i.e. global NOAA-NCEP pressure level reanalysis data archives reprocessed into the HYSPLIT compatible format (Draxler and Rolph, 2003; Rolph et al., 2017; Rozwadowska et al., 2010). The trajectory calculations were based on data from the Global Data Assimilation System (GDAS) of the National Weather Service's National Centre for Environmental Prediction (NCEP). The global data are given on a latitude–longitude grid (2.5 degrees) at 17 pressure levels, and the time resolution of the data is 6 h (Air Resources Laboratory (ARL), 2003). Five-day (120-h) backward trajectories arriving at 62.19°S, 58.52°W and 500 and 1000 m AGL were run every 6 h (ending at 12:00, 18:00, 00:00, 06:00 UTC) (Chand et al., 2010; Cristofanelli et al., 2011; Gao et al., 2020; Hondula et al., 2010; Rolph et al., 2017) over the sampling period, to give a total of 736 trajectories for the six months (August 6th 2016 to February 6th 2017) and 124 trajectories for the 30th days preceding sampling. Six clusters' mean trajectories were calculated based on total spatial variance analysis for a half-year period, and four clusters' mean trajectories for 30th days (Draxler et al., 2020; Draxler and Rolph, 2003; Stein et al., 2015).

4. Results

4.1. Basic inorganic ions and total organic carbon analysis

The analysed samples are characterised by low total concentrations of measured ions ranging from 1.92 to 25.7 mg/L (blank sample: 0.71 mg/L). The sums of cations concentrations in the snow samples ranged from 0.23 mg/L to 6.71 mg/L, while sums of anions concentrations ranged from 0.74 mg/L to 19.0 mg/L. The values of the determined ions for all the analysed samples are presented in Table 1. The analyses revealed that Cl^-, Na^+ and SO_4^{2-} clearly dominate in the inorganic chemical composition of the analysed snow. However, for some ions (NH_4^+, Li^+, F^-, NO_2^-, Br^-, PO_4^{3-}) the concentration was below the limit detection in all studied samples. Fig. 2A and B presents the percentage of individual ions in the total composition of cations and anions. Cl^- ions constituted 67.0% of the total sums of anions. In turn, SO_4^{2-} ions constituted 14.5% of anions, and Na^+ 59.7% of all cations. The percentage of $nssSO_4^{2-}$ was small for snow samples collected on the western coast of Admiralty Bay and ranged from 0.03% to 1.97%. Particularly noteworthy are the NO_3^- concentrations that were detected in snow samples E2, E4 and E5. The concentration values of these ions ranged from 1.1 to 5.0 mg/L, and NO_3^- ions constituted 18.5% of all anions. In addition, higher concentrations of Mg^{2+} and Ca^{2+} should be noted compared to K^+, NH_4^+ and Li^+ cations. The range of Mg^{2+} concentrations in the snow samples ranged from 0.09 to 4.60 mg/L, while the Ca^{2+} concentrations ranged from 0.07 to 0.57 mg/L.

Total organic carbon (TOC) content in all snow samples taken at the western coast of Admiralty Bay was determined (Table 1, Fig. S1). Their values ranged from 0.33 to 0.77 mg/L. The TOC value for the blank was 0.33 mg/L. The lowest TOC concentration was found in the E1 sample in which its concentration was equal to the concentration in the blank

Table 1
Ion concentrations and TOC in snow samples collected at the western shore of Admiralty Bay.

Sample name	Sample point elevation	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	TOC
	m a.s.l.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
W1	298.28	5.9	0.15	0.09	0.57	17	<LOD	2.0	0.62
W2	387.79	0.53	<LOD	<LOD	<LOD	1.6	<LOD	<LOD	0.46
W3	462.67	1.2	<LOD	0.18	0.27	3.7	<LOD	0.44	0.50
W4	60.88	0.32	<LOD	4.6	0.42	0.96	<LOD	0.31	0.77
E1	108.95	0.21	<LOD	0.11	0.11	0.54	<LOD	0.20	0.33
E2	124.46	0.23	<LOD	<LOD	<LOD	0.37	1.1	0.22	0.41
E3	172.38	0.56	<LOD	<LOD	0.24	1.1	<LOD	0.27	0.45
E4	202.41	0.26	<LOD	<LOD	0.07	0.31	1.6	0.36	0.43
E5	220.82	1.6	<LOD	<LOD	0.43	2.3	5.0	2.2	0.36
BLANK		0.21	<LOD	<LOD	<LOD	0.43	<LOD	0.07	0.33
LOD		0.01	0.01	0.01	0.01	0.06	0.014	0.05	0.01
LOQ		0.03	0.03	0.03	0.03	0.18	0.042	0.15	0.03

LOD – limit of detection; LOQ – limit of quantification.

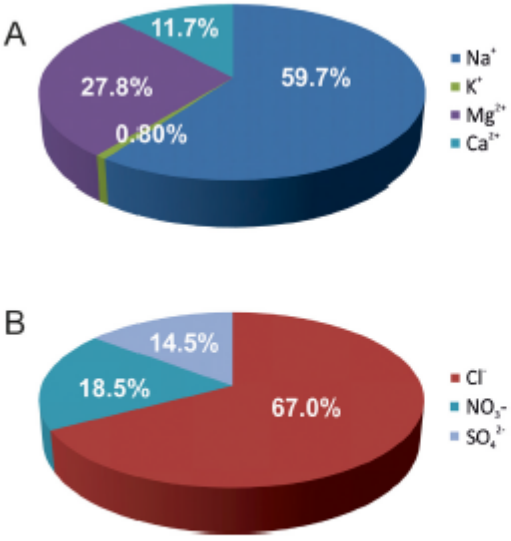


Fig. 2. Percentage of individual ions in the total of: A. cations; B. anions.

sample. The highest TOC values were found for sample W4 (0.77 mg/L), W1 (0.62 mg/L) and W3 (0.50 mg/L), respectively.

4.2. Analysis of metals and non-metals

As a result of the analysis of snow samples for metals and non-metals, 17 out of 18 elements were identified and determined (Table 2). The only one that was not found in any of the samples or was below the limit of detection was Cu. It is noteworthy that the concentrations of selected elements in the snow samples were close to the concentrations in the BLANK sample, and sometimes were even lower (Ag, As, Ba, Cd, Co, Cr, Fe, Mo, Ni, Pb, Sb). The higher concentration in selected snow samples compared to the BLANK was observed in Al, Cr, Fe, Mn, Sr and Zn.

In the case of some elements, an effect was observed in which their concentrations at most points were similar to the BLANK samples, but individual snow samples were characterised by concentration levels that were several to several dozen times higher. Al concentration was the highest at points closest to the Arctowski and Carlini research stations (W1 and W4). For Al, they were respectively 6.29 and 5.76 μg/L at points W1 and W4. The concentration of Zn was elevated relative to other points in W3 (where it was 45.1 μg/L) and in E2 (where it was 30.4 μg/L).

During the research, it was found that V is characterised by several times higher concentrations compared to the BLANK sample in almost all points except point W1 (closest to the Arctowski research station), where the concentrations of these chemical species were several dozen times higher. The concentration of V at this point was 1.09 μg/L. Of these elements, the lowest concentration was identified for V (0.0091 μg/L) at point W3. A similar tendency can be observed by analysing the concentrations of Fe and Sr, the highest concentrations of which were found in samples W4 for Fe (6.52 μg/L) and W1 for Sr (4.10 μg/L). For each of these two chemical entities, points were identified where the element concentration was lower than that of the BLANK sample. These points were W3, E1 and E5 for Fe, and point W2 for Sr.

The concentrations of Sb and Se in the Antarctic snow samples were relatively low. However, when analysing the concentrations in pristine environments, attention should be paid to even the smallest fluctuations and differences in the levels of the elements' concentrations. The concentration of Sb was highest in sample W1, amounting to 0.49 μg/L, and slightly lower in points W2, E1 and E3, being 0.056, 0.057 and 0.033 μg/L, respectively. In the other samples, the concentration of this element was similar to the BLANK sample. The Se concentration was above the limit of detection in samples W1 (0.071 μg/L), W4 (0.16 μg/L) and E4 (0.074 μg/L).

In the researched samples very strong positive correlation ($0.8 < |r| \leq 1$) were indicated between TOC and Al, Fe, Se and strong ($0.6 < |r| \leq 0.8$) between TOC and Mn, Mo (Table S2). The following very strong positive correlations occurred: between Al and Fe, Mo; between Ba and Ag; between Co and Cd, Zn; between Sb and Cr, Sr, V. Moreover, the following strong correlations are visible: Al and Mn, Sb, Sr, V; Ba and Pb; Cd and Zn; Fe and Mo; Mo and Sb, Sr, V.

4.3. Polycyclic aromatic hydrocarbons analysis

During the study of PAH concentrations in snow collected on the western coast of Admiralty Bay, three chemical compounds from this

Table 2
Levels of analysed elements in snow samples collected at the western shore of Admiralty Bay (values double those of the BLANK sample, or higher, are underlined).

Sample point name	Ag	Al	As	Ba	Cd	Co	Cr	Fe	Mn	Mo	Ni	Pb	Sb	Se	Sr	V	Zn
	μg/L																
W1	0.09	6.29	1.42	0.09	0.0037	1.51	0.14	3.90	0.23	0.057	0.28[a] (<LOQ)	1.12	0.49	0.071[a] (<LOQ)	4.10	1.09	6.42
W2	0.09	1.65	<LOD	0.09	0.0039	0.4	0.041	2.32	1.56	0.0082[a] (<LOQ)	<LOD	1.06	0.056	<LOD	0.57	0.019	15.9
W3	0.09	2.08	<LOD	0.23	0.0074	3.26	0.049	2.28	0.45	0.013[a] (<LOQ)	<LOD	1.09	0.018	<LOD	1.76	0.0091	45.1
W4	0.09	5.76	0.04[a] (<LOQ)	0.14	<LOD	0.43	0.04	6.52	0.39	0.052	<LOD	1.10	0.023	0.16	1.08	0.14	4.64
E1	0.09	1.59	0.08	0.13	0.0061	1.01	0.064	2.20	1.74	0.0207	<LOD	1.07	0.057	<LOD	0.95	0.042	12.8
E2	0.09	2.77	<LOD	0.27	0.012	2.81	0.0601	2.54	1.80	0.023	<LOD	1.07	0.03	<LOD	1.31	0.036	30.4
E3	0.09	1.83	0.06	0.11	0.0060	0.99	0.084	2.73	3.05	0.023	<LOD	1.06	0.033	<LOD	1.38	0.063	11.6
E4	0.09	1.75	0.07	0.09	0.0015[a] (<LOQ)	0.28	0.045	2.58	1.69	0.028	<LOD	1.05	0.017	0.074	1.29	0.092	5.09
E5	0.1	1.70	0.05[a] (<LOQ)	0.76	0.0034	0.44	0.053	1.84	1.58	0.0301	<LOD	1.15	0.026	<LOD	0.99	0.057	8.93
BLANK	0.09	1.68	<LOD	0.49	0.0096	8.17	0.0602	2.29	0.72	0.013[a] (<LOQ)	<LOD	1.06	0.018	<LOD	0.73	0.0102	9.45
LOD	0.0033	0.03	0.018	0.0039	0.0008	0.0040	0.0034	0.085	0.020	0.0047	0.21	0.088	0.0017	0.063	0.0093	0.0016	0.15
LOQ	0.011	0.099	0.059	0.013	0.0026	0.013	0.011	0.28	0.067	0.016	0.72	0.29	0.0056	0.21	0.031	0.0052	0.49

LOD – limit of detection; LOQ – limit of quantification.
[a] Samples analysed in triplicate with the RSD <5%.

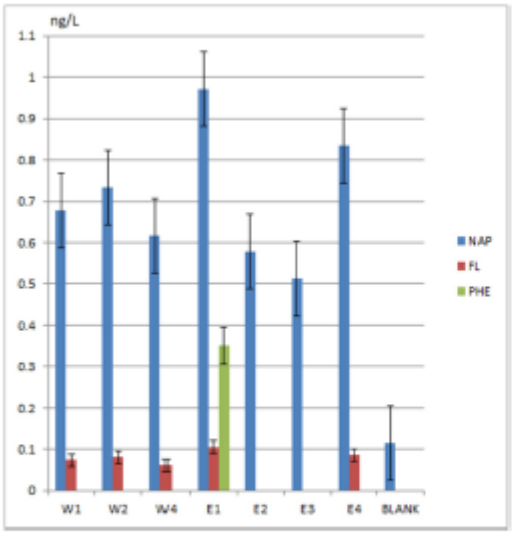


Fig. 3. PAH concentration values in individual snow samples (ng/L). Abbreviations: NAP-naphthalene; FL-fluorene; PHE-phenanthrene.

group were identified: naphthalene, fluorene, phenanthrene (Fig. 3, Table S3). The sum of PAHs in individual snow samples is relatively low and ranges from 0.51 to 1.40 ng/L. Naphthalene has the largest percentage in the content of PAHs. Its concentration level in environmental samples ranged from 0.51 to 0.97 ng/L, while in the blank sample 0.11 ng/L was found. Unlike the other samples, the fluorene concentration was below the limit of detection (LOD) in the E2 and E3 snow samples. Fluorene concentrations ranged from 0.06 to 0.11 ng/L. In addition, phenanthrene in the E1 sample was 0.35 ng/L, which was equal to the LOD. Due to the properties of five- and six-ring PAHs, it was assumed that their presence in snow samples would not be detected or would be below the LOD. These assumptions were confirmed by the results obtained. Five- and six-ring PAHs have lower volatility and water solubility compared to other PAHs.

4.4. Origin of air masses

During the period of August 2016 to February 2017, the air masses flowing into King George Island originated mostly from the Antarctic area, – mainly the South Ocean (latitudes above 60°S) (Fig. 4A). Circumpolar air circulation was represented by three clusters of trajectories constituting a total of 58% of air masses computed for 500 m a.g.l. and 54% for air masses computed for 1000 m a.g.l. However, during the analysed six months, air masses forming over southern parts of South America also come to KGI, with the frequency of this sourcing area ranging from 1 to 10% (Fig. 4B). The calculation of frequencies of air masses for the period of 30th days preceding sampling show that, for three clusters of trajectories, air masses originated over the South Ocean. These clusters of trajectories cover 86% of all air masses at 500 m a.g.l., and 67% at 1000 m a.g.l. One should note that the cluster representing trajectories that originated in the area of South America shows that air masses from the inhabited area take approximately two days to be transported into KGI.

5. Discussion

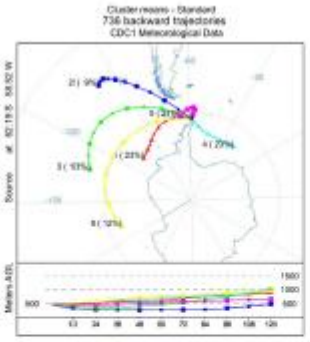
5.1. Inorganic chemicals in snow cover and its sources

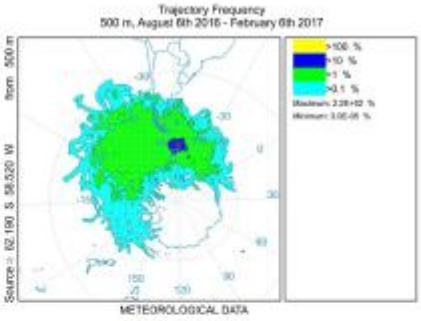
Szopińska et al. (2018), (2019), and Potapowicz et al. (submitted, Part 1) reported results of chemical analysis in the forefield of the Warszawa Icefield at the western shore of Admiralty Bay. This study aims at identifying possible sources of chemicals obtained in the ice-free areas. Previous results of fresh waters' chemistry showed low mineralisation of creeks fed by the glacier or snowmelt (Szopińska et al., 2018). Analysed snow samples indicate similarly low mineralisation not exceeding 30 mg/L. The study sites at the Warszawa Icefield are elevated at between 60.88 and 462.67 m a.s.l., and are under strong marine influence, which is confirmed by the highest share of Na^+ and Cl^- compared to the other cations and anions. The high influence of marine factors is confirmed by the prevalence of air masses originating over the South Ocean among the air masses incoming to the study area (this study, Szumińska et al., 2018). A prevalence of marine-source ions in snow were reported widely in different sites of Antarctica (e.g. Ali et al., 2010; Dixon et al., 2013, 2005; Kaspari et al., 2005). Bertler et al. (2005) show a wide spatial and temporal variability of snow-cover and ice-core chemistry across the Antarctic continent and Maritime Antarctica and its reverse correlation with selected geographical features, i.e. elevation and distance from the sea. However, it is worth noting that in the case of the studied samples collected in the Warszawa Icefield there is no simple dependence between elevation and Na^+ and Cl^- (Table 1). The highest values of these ions are observed at the highest elevated sampling points (E1, E3 and E5), which is associated with close proximity to the sea. Furthermore, the high elevation of these sites meant that there were no orographic barriers that might limit the influence of marine aerosols. The role of orographic barriers in shaping precipitation and ice chemistry along the Antarctic Peninsula was mentioned recently by Fernandoy et al. (2018).

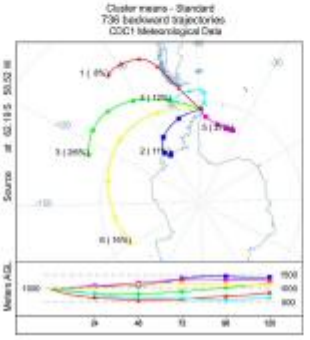
The studied snow samples are characterised by a very low share of $nssSO_4^{2-}$, ranging from 0.03% to 1.97%, which is several times lower than the values obtained in fresh water at the western shore of Admiralty Bay (20.3% to 70.3%) (Szopińska et al., 2018). Jiankang et al. (2001) notes that the values of $nssSO_4^{2-}$ in snow and firn is characterised by temporal variation, which is related to the influence of non-marine factors during snow accumulation, and seasonal and annual weather changes. Furthermore, cold conditions limit the leaching of ions and elements. Warmer conditions, conversely, support more intensive percolation and leaching of chemicals into deeper layers (Jiankang et al., 2001). The chemical status of snow pack depends as well on the solubility of stored compounds (Kozioł et al., 2017; Meyer and Wania, 2011). As we mentioned before, surface snow samples in this study are characterised by very low mineralisation, which may be the effect of the relatively warm summer conditions of 2017 (Potapowicz et al., submitted, Part 1). In 2017, and the preceding 2016, the mean annual temperature on the King George Island was approximately 1 °C higher than the preceding years of 2013–2015 (Plenzler et al., 2019). Temperatures observed in 2016 (−0.9 °C) and 2017 (−1.4 °C) in Arctowski Polish Polar Station were also higher compared to long-term data from the period of 1977–1998 (−1.6 °C). In particular, warm conditions in December 2016 and January 2017 (mean temperatures of 0.9 °C higher than data from 1997 to 1998) supported vertical percolation of chemicals into deeper layers and may be the reason for the generally low mineralisation of studied surface snow samples. The sources of metals in surface snow on glaciers may be from either natural (local rock dust, marine aerosol, volcanic activity) or anthropogenic sources (e.g., local impurities in combusted fuel and waste incineration) (Kozioł et al., 2021; Pérez-Rodríguez et al., 2019). Moreover, snow chemistry is under the influence of long-range

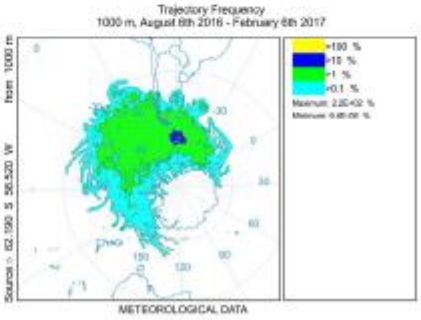
Fig. 4. Air mass frequencies at 500 and 1000 m from periods: A – August 6th 2016 to February 6th 2017; B – January 6th to February 6th 2017 (calculated with the NOAA HySPLIT model based on Global Data Assimilation System meteorological data – Hybrid Single-Particle Lagrangian Integrated Trajectory, version 5).

A









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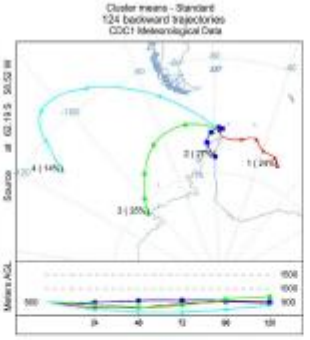

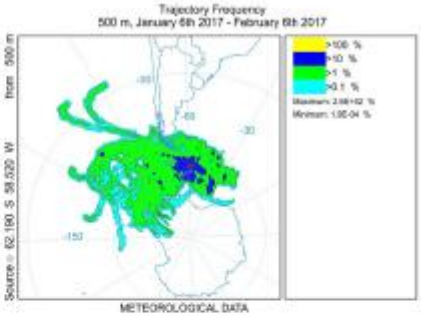

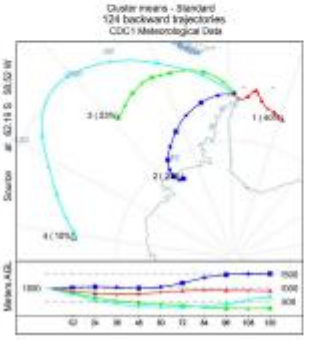

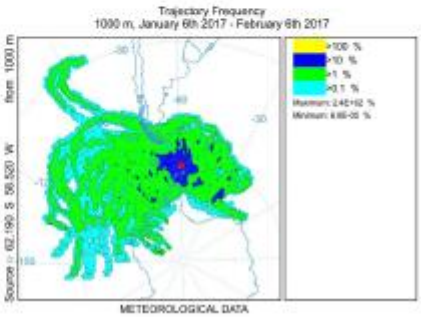

atmospheric transport, which should be recognised as a mixed source, due to the fact that both natural (e.g. volcanic) and anthropogenic contaminants may be transported into Antarctica from remote areas (Bargagli, 2016; Hara et al., 2019; McConnell et al., 2014), and be stored in snow pack and ice (Chambers et al., 2014; Pérez-Rodríguez et al., 2019). Taking into account that concentrations of metals in the snow pack on the glaciers depends on the season of deposition (Kozioł et al., 2021), the obtained results are quantitative temporal evidence of the chemical status of snow pack, being the result of deposition conditions and post-sediment leaching processes (Jiankang et al., 2001). The low content of $nssSO_4^{2-}$ in studied samples from the Warszawa Icefield shows the possibility of (1) intensive leaching of elements originating from local dust and LRAT, and/or (2) transfer into deeper parts of the snow pack during freeze–thaw processes, and/or (3) small temporal delivery of contaminants by long-range atmospheric transport (LRAT). The obtained results related to origins of air masses show that frequency of inflow from remote inhabited areas ranges from 1 to 10% during the half year preceding sampling. South America was recognised as a possible source of contaminants transported by LRAT to the Antarctic Peninsula region (both natural and anthropogenic) by Lee et al. (2007), Pereira et al. (2006) and Szopińska et al. (2019). Fuoco et al. (2012) pointed out the high share of $nssSO_4^{2-}$ in the ice horizons at Talos Dome (Victoria Land) associated with strong volcanic events in remote regions. Low content of $nssSO_4^{2-}$ is also associated with a low content of Fe. Iron originating from sulphide minerals accompanies $nssSO_4^{2-}$ (Moses et al., 1987). In the studied snow samples, low content of $nssSO_4^{2-}$ accompanies low content of Fe (higher compared to BLANK only at sites W1 and W4), which suggests a negligible share of elements of rock and volcanic origin. On the other hand, in the studied snow samples, higher values of Al and V than of other elements have been found. Previous research shows that Fe and Al are represented at high concentrations in fresh water fed by glacier thawing and snow samples at glacier forefields (Szopińska et al., 2018), because these elements are the typical product of mechanical rock weathering in the studied region (Birkenmajer, 1996). However, the high content of Fe in water at the beginning of the summer season and its decreasing over the next months (Szopińska et al., 2018) may be the effect of the high mobility of Fe in the glacial meltwater (Hopwood et al., 2014). The highest values of Fe in the studied surface snow samples were obtained at the W1 and W4 site, which is located at the edge of the glacier icefield; similarly, the highest contents were observed at sites W1 and W4 for Al and K, and at W1 for Mg. The observed increase in studied metals at sites close to the glacier forefields is the effect of more intensive local dust in these areas. The low content of elements not associated with aerosols may also be the effect of the prevalence of air masses that originated over Antarctica at the time preceding sampling time. The frequency of air masses incoming from remote areas ranges from 1 to 10% for the period of September 2016 to February 2017 (based on 5-day trajectories). Previous research obtained for the period of September 2015 to August 2017 shows that the frequency of incoming air masses originating outside Antarctica amounted to approx. 50% for 10-day trajectories (Szopińska et al., 2018). Therefore, the time preceding sampling is characterised by LRAT being limited compared to the subsequent and previous months (Potapowicz et al., submitted, Part 1; Szuminska et al., 2018).

Special interest should be paid to chemicals, both natural and anthropogenic of possible negative influence on Antarctic environment. Mishra et al. (2004), based on an investigation of aerosols on King George Island (in the vicinity of King Sejong station) distinguished an anthropogenic group of contaminants of local sources (the station's activity and logistics) and LRAT including: Bi, Cd, Co, Cr, Cu, Ni, V and Zn. However, a study of cryoconites from the Fildes Peninsula indicated that some elements mentioned above (Cr, Pb, Zn, Ni) have a volcanic origin; and only Cd and Cu were accumulated as a result of anthropogenic activity (fuel spills and paintwork in the Antarctic station areas) (Polyakov et al., 2020). The most recent studies obtained in the South Shetland Islands showed, that local volcanic activity in Deception Island may be an important source of Hg in fresh waters, sediments and snow (Mão de Ferro et al., 2014), and one of the sources of As in fresh waters (Mão de Ferro et al., 2013) due to active fumaroles. Moreover, ongoing hydrothermal activity may increase Cd values in marine waters (Mão de Ferro et al., 2013). Therefore, local volcanic sources of contaminants in the South Shetland Islands environment should also be taking into consideration.

In this study, slight contamination by As, Cr, Ni, Sb, Sr and V (at concentrations of 1.42, 0.14, 0.28, 0.49, 4.10, 1.09 μg/L, respectively) were observed in snow samples at site W1 at the edge of the glacier icefield and close to Arctowski station, and Zn and Sr (5.09–45.1 μg/L, 0.57–4.10 μg/L, respectively) also at other sampling points. Arsenic was present in all samples except those from the highest points, W3, W2 and E2, and manganese also occurred in samples from Ecology Glacier. Cadmium in the studied snow samples was in the range of 0.0015–0.012 μg/L (Table 2), which can be considered a natural level for the Antarctic region (Hong et al., 2004). However, there is no evidence of contamination by anthropogenic cadmium in sediment samples collected in 2016 from the ice-free areas at the western shore of Admiralty Bay (Potapowicz et al., 2020). Furthermore, in flowing water, increased values of Sr, Cu and Zn were observed in creeks located close to Arctowski station, and a very strong correlation ($0.8 < |r| \leq 1$) between (Zn and Cu), and between (Co and Mn) (Szopińska et al., 2018). Therefore, some trace metals observed in surface snow at the Warszawa Icefield may be evidence of a temporal anthropogenic influence of the nearest stations and scientific logistics (snowmobiles and helicopters). One should note that a very high or high correlation is visible between these metals in the studied samples. Trace elements observed across the transect (Mn, Sr, V, Zn) should be linked with the long-range sources. Dias da Cunha et al. (2009), based on snow samples, found that increased V and Pb values occurred widely at several points along the shore of Admiralty Bay. The authors concluded that these elements originated during fuel combustion by vehicles and heating systems. The presence of these contaminants in aerosols observed by Dias da Cunha et al. (2009) in this area may have been caused by increasing human activity in the King George Island during recent decades.

5.2. PAHs in snow cover and its long-term environmental impact

Though at low or medium concentrations, PAHs are among the most widespread contaminants in Antarctica. Brought in by via atmospheric local and long-range transport (Fuoco et al., 2012; Martins et al., 2010), they are delivered by aerosols and precipitation and accumulated in abiotic environments and the subsequent links in the food chain of Antarctic biota (Cabrerizo et al., 2012; Potapowicz et al., 2019). The special attention focused on PAHs is a result of its toxicity and carcinogenic and mutagenic influence on living organisms (Yang et al., 2015). Furthermore, low temperatures and limited solar radiation cause the longer environmental residence time of organic pollutants here, as compared to lower latitudes (Kukucka et al., 2010).

Summaries of research considering persistent organic pollutants have been presented in previous works by Szopińska et al. (2017) and Potapowicz et al. (2019). The authors pointed out the occurrence of PAHs in abiotic and biotic environments in different regions of Antarctica, including the Antarctic Peninsula and South Shetland Islands. In this study the levels of PAHs in snow and ice samples from different Antarctic sites were compared (Table 3).

The presented data show the high variability of ΣPAHs concentrations in snow samples, ranging from 0.11 ng/L in the Warszawa Icefield (King George Island) (this study) to 272.29 ng/L on the Fildes Peninsula (King George Island) (Na et al., 2011). The highest values of ΣPAHs observed in Fildes Peninsula were connected by the authors mainly with atmospheric transport and combustion of fuel. Several hotspots of pollutants related to scientific stations were also described for this area by Amaro et al. (2015) and Padeiro et al. (2016).

Table 3
Example concentration ranges for total PAHs in different snow samples in Antarctica.

Sampling area	Σ PAHs	Type of sample	PAH species (prevailing)	Source	Reference
Ekström Ice Shelf, Atka Bay, north-eastern Weddell Sea	23.7–188 ng/L (snow pit of 1.8 m depth) 23.7 ng/L (surface)	Surface snow	NAP, 1M-NAP, 2M-NAP, PHE	Local anthropogenic sources	Kukucka et al., 2010
Fildes Peninsula (KGI)	52.15–272.29 ng/L	Snow	NAP, Fl, PHE, ACP	Long range transport – anthropogenic sources, local anthropogenic sources	Na et al., 2011
Talos Dome, Victoria Land, EA	0.35–4.6 ng/L (core of 52 m depth) 3.0–3.4 ng/L (surface)	Snow, firn core	PHE, FLA, PYR	Volcanic eruptions; Long range transport – anthropogenic sources	Fuoco et al., 2012
Vegetation Island, Vitoria Land, EA	0.65 ng/L	Surface snow	PHE, BaP	Long range transport – anthropogenic sources with secondary local redistribution, local anthropogenic sources	Vecchiato et al., 2015
Faraglione camp, Vitoria Land, EA	1.6 ng/L		PHE, Fl, BaP, FLU		
David Glacier, Vitoria Land, EA	14 ng/L		NAP, PHE, Fl, ACP, FLU		
Mid Point, Vitoria Land, EA	140 ng/L		NAP, Fl, ACP, PHE, FLU		
GVS Itase, Vitoria Land, EA	1.2 ng/L		PHE, Fl, BaP, FLU		
Western shore of Admiralty Bay (KGI), glacier forefield	6.78 ng/L	Surface snow	Fl, CHY, BaP	Long range transport – anthropogenic sources, local anthropogenic sources	Szopińska et al., 2019
Western shore of Admiralty Bay (KGI), Warszawa Glacier	0.11–1.4 ng/L	Surface snow	NAP, Fl, PHE	Long range transport – anthropogenic sources, local anthropogenic sources	This study

PHE – phenanthrene, FL – fluorene FLA – fluoranthene, PYR – pyrene, BaP – benzo(a)pyrene, FL – fluorene, NAP – naphthalene, 1M-NAP – 1-methylnaphthalene, 2M-NAP – 2-methylnaphthalene, ACP – acenaphtene, CHY – chrysene; KGI – King George Island, EA – East Antarctica.

Special attention should be paid to results obtained by Fuoco et al. (2012), which described high vertical variability of ΣPAHs concentrations in a 52-metre-depth ice core in Talos Dome (Victoria Land). The occurrence of PAHs throughout the whole ice core reveals their uninterrupted delivery to Antarctica, even in pre-industrial times. In the horizons deeper than 32.2 m (accumulated before 1600) ΣPAHs levels were in the range 0.35–1.0 ng/L. The highest concentration (4.6 ng/L) has been found in an ice horizon accumulated during the eruption of an Indonesian volcano – Tambora (in 1815). Furthermore, the authors recorded an overall 50% increase in PAH concentrations between 1930 and 2002 (increasing by about 0.013 ng/L/year). Results obtained by Fuoco et al. (2012) and other authors (Table 3) confirm the high temporal and spatial variability of delivery of PAHs into Antarctica and both natural (volcanic eruptions) and anthropogenic sources (combustion of biomass, fossil fuels, oil spills).

The surface snow samples presented in this study are characterised by low concentrations of PAHs compared to the results of other authors (Table 3). However, one should note that Szopińska et al. (2019) found that ΣPAHs concentrations in the creeks flowing in the glacier forefields reached a value of 427 ng/L, and 1365 ng/L in creeks located close to the Arctowski station (Fig. 5). Szopińska et al. (2019) and Potapowicz et al. (submitted, Part 1) have observed that temporal changes in PAH concentrations were caused by their being delivered from glacier and snow melt, and also by its remobilisation in soils during the summer. Moreover, the map of ΣPAH distributions presented by Potapowicz et al. (2019) shows that study points across the whole of Antarctica are mainly located in the vicinity of scientific stations. However, PAHs recorded in all snow samples along the transect at the Warszawa Icefield, despite the slight LRAT in the months preceding sampling, may confirm the thesis that POPs are widespread in Antarctica, and their concentrations in particular horizons depend on temporal changes in local and global PAH distributions. Furthermore, a slight influence of local factors (scientific station activity) is visible in the site close to the Arctowski station (E1). The phenanthrene that occurred at this point may be an effect of fuel combustion in the vicinity of the station. Apart from annual scientific activity, the study area is also under growing human impact connected with tourist cruises (2000 tourists in 2018) (Wilkońska et al., 2020). It is noteworthy that a similar composition of PAHs, with a prevalence of naphthalene, fluoranthene and phenanthrene, has been found on the Fildes Peninsula (Na et al., 2011). Naphthalene and phenanthrene prevailed in five out of ten study sites (Kukucka et al., 2010; Na et al., 2011; Vecchiato et al., 2015), located both in continental and Maritime Antarctica (Table 3). These low-molecular-weight, two- and three-ring PAHs may be connected with local and long-range sources. The higher molecular weight PAHs (4- and 5-ring), associated with combustion processes (Martins et al., 2010), were absent in studied snow samples from the Warszawa Icefield. However, in samples collected at the Baranowski Glacier forefield in 2016, benzo(a)pyrene and chrysene were detected (Szopińska et al., 2019). These PAHs were also indicated in creeks on ice-free areas in the vicinity of Arctowski station. Potapowicz et al. (submitted, Part 1) pointed out a domination of naphthalene, phenanthrene and anthracene in fresh and marine waters and sediments in these areas. Both works show pyrogenic and petrogenic sources of PAHs, and a time-varying influence of local sources. Strong temporal pressure of station operation has been documented as well by Martins et al. (2010) in marine sediments at Admiralty Bay (Fig. 5). Increasing concentrations of PAHs have been documented by authors since the 1980s, reflecting the increase in human activity in the area (increases in fossil fuel consumption, combustion of organic matter and petroleum derivatives, and input of wastewater effluent).

Cryogenic environments may be a sink for contaminants from global and local sources. The scheme of ΣPAHs distributions at the western shore of Admiralty Bay (Fig. 5) confirms its complex pattern, where particular elements of the abiotic environment may be places of direct accumulation of this contaminant or constitute part of the transitional path. One should note the possibility of the sinking of these pollutants in terrestrial and marine sediments. Although PAH background levels in the inputs (air, precipitation) are generally low (Fig. 5), its accumulation may have increased during historical volcanic events (Fuoco et al., 2012), periods of intense station activity and shipping (Martins et al., 2010), or incidental events (Vecchiato et al., 2015). Glacier ice horizons enriched in PAHs by historic volcanic episodes (Fuoco et al., 2012) may be important secondary sources of these carcinogenic compounds being increased by rising glacier retreat in Maritime Antarctica (Pudełko et al., 2018; Szilo and Bialik, 2018). This phenomenon (leaching of historical volcanic horizons) may be the reason for the high values of ΣPAHs (427 ng/L) previously observed by Szopińska et al. (2019) in the direct inflow from the Sphinx Glacier snout.

Previous analyses of air mass trajectories show relatively frequent (31%) influx of air masses from southern South America, which is one of the volcanically more active areas (Szumińska et al., 2018). According to Global Volcanism Program data (www.volcano.si.edu), in the months preceding surface snow sampling in this study, several volcanoes were

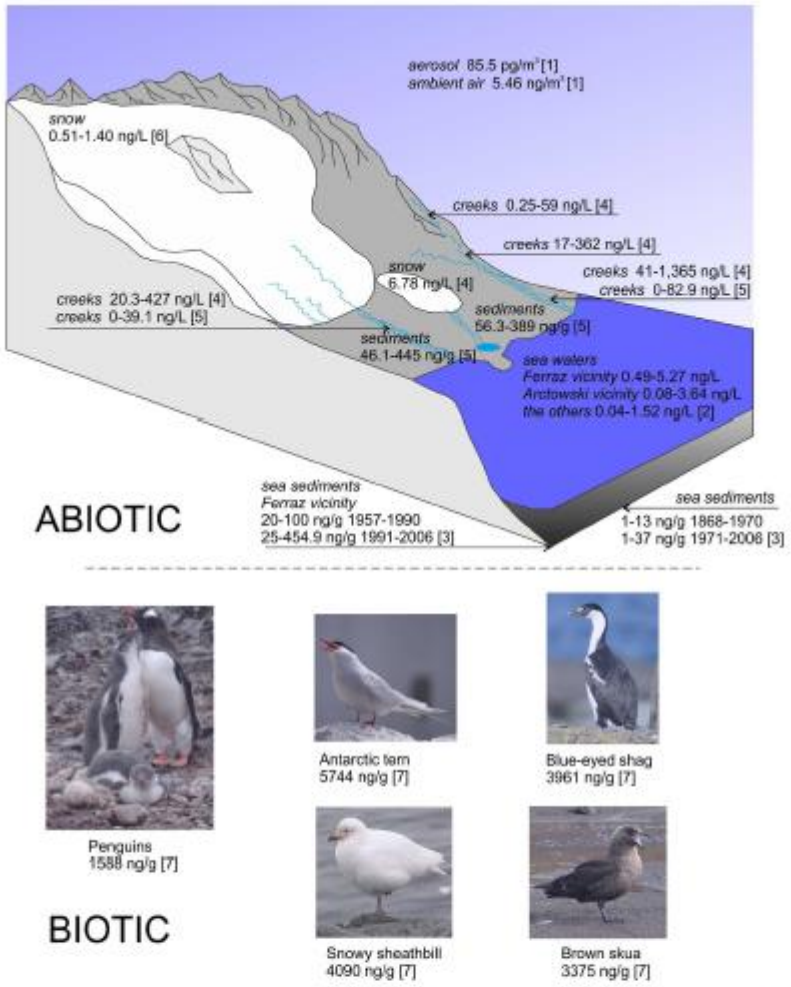

Fig. 5. ΣPAHs concentrations in abiotic and biotic environments at Admiralty Bay (King George Island): aerosol pg/m³, air – ng/m³, water and snow samples – ng/L, sediment samples – ng/g, Antarctic seabirds' fat tissues – ng/g lipid weight (sources of data: [1] Cabrerizo et al. (2014) – Supporting Information; [2] Bicego et al. (1996); [3] Martins et al. (2010); [4] Szopińska et al. (2019); [5] Potapowicz et al. (submitted, Part 1); [6] this study; [7] Taniguchi et al. (2009)).

active in South America (i.e. Copahue, Nevados de Chilian, Sabancaya, Villarica). In the case of the Sabancaya volcano, one of the largest explosions was observed in November 2016 (www.volcano.si.edu). Furthermore, research obtained by Lee et al. (2007) show that about 10% of tephra found in Holocene Lake on KGI originated from distant volcanoes. The confirmed role of South America in shaping air masses incoming to KGI (Fernandoy et al., 2018; Lee et al., 2007; Pereira et al., 2006) shows the possibility of an influx of PAHs related to volcanic activity and combustion of fuels in that region prior to sampling. However, taking into consideration up-to-date results related to the influence of contemporary local volcanic sources on Hg and As concentration in snow and waters at the nearest island of Deception (Milo de Ferro et al., 2014, 2013) and Hg concentration in soils on the Byers Peninsula (Livingstone Island) (Pérez-Rodríguez et al., 2019) it is worth considering a possible local-volcanic source of PAHs on the South Shetland Islands.

The remobilisation of stored PAHs is a predictable potential effect of the observed climate changes (Bockheim et al., 2013; Turner et al., 2005; Vaughan et al., 2003). Temporal increases in PAH accumulations cause increasing amounts of PAHs in Antarctica, and, in connection with its increasing release from snow and ice, may increase its negative influence on living organisms (e.g. via constant accumulation of this pollution in tissues and fat) (Fig. 5). Its negative influence has been observed inter alia as carcinogenic and for damaging liver cells of *Notothenia corriceps* (Curtosi et al., 2009), and toxic for sea urchins immediately subsequent to hatching (Alexander et al., 2017) in Antarctica.

6. Conclusions

Only a few published studies have considered pollution in snow on the Antarctic continent and Maritime Antarctica. The results obtained

at the Warszawa Icefield confirmed the occurrence of chemicals referred to as contaminants in snow cover, the limited influence of the nearest scientific stations, and the mainly atmospheric origin of observed pollutants (from regional and LRAT sources). The study shows low concentrations of inorganic elements (<30 mg/L), TOC (<1 mg/L) and PAHs (0.11–1.4 ng/L) in snow samples collected during the 2017 austral summer. The low concentrations may be the effect of low temporal delivery of pollutants and/or leaching into deeper horizons. Despite low pollutant levels, a slight increase in ΣPAHs and trace-metal concentrations has been observed at the marginal parts of the icefield, which is the result of the influence of scientific stations and more effective local dust in these areas. Naphthalene and fluorene predominated across all the study sites, except that site close to the Arctowski station, where phenanthrene was observed in snow. All three compounds are low Molecular Weigh PAHs, which are present in diesel. Hence, they may originate from either local diesel combustion or from long-range atmospheric transport, or both. The pattern of PAHs at Admiralty Bay shows an accumulation in subsequent environments via the following path: snow/ice → fresh water/terrestrial sediments → marine water/marine sediments → Antarctic biota.

Moreover, a higher diversity of marine-origin ions (Na^+ and Cl^-) was observed relative to previous research, and the influence of orographic barriers on its delivery has been pointed out. One should note that local topography may be an important factor in the deposition of aerosols at the dynamically changed ice-free areas of Maritime Antarctica.

The risk associated with rapid glacier thawing and the release of pollutants from ice indicates the need for research into pollutants in surface snow and ice cores on King George Island. The potential negative effect of the presence of heavy metals and hydrocarbons in the snow and ice should be investigated in detail during further research. Comparison of the presence of PAHs in different types of environments would help to indicate the sources of pollutants, and to assess the risk of its remobilisation. Furthermore, particularly in the close vicinity of Arctowski scientific station, the risk of local emission of pollutants has been increased by the construction of new facilities started at 2020. Therefore, pollutants need to be monitored in different environments.

CRediT authorship contribution statement

Danuta Szumińska: Conceptualization, Methodology, Software, Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Joanna Potapowicz:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Writing – review & editing, Visualization, Supervision, Project administration. **Małgorzata Szopińska:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing. **Sebastian Czapiewski:** Software, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. **Ulrike Falk:** Investigation, Writing – review & editing. **Marcin Frankowski:** Methodology, Software, Formal analysis, Writing – review & editing. **Żaneta Polkowska:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing – review& editing, Project administration, Funding acquisition.

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

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7.3 Verification of detailed hypothesis 3: Untreated wastewater discharge into Admiralty Bay constitutes a threat to the marine Antarctic environment

Inappropriate discharge of wastewater into Antarctica's fragile marine ecosystems can result in the introduction of not only persistent organic pollutants and other organic and inorganic pollutants but also non-indigenous microorganisms, including human-associated pathogens and viruses [87]. For Antarctica, wastewater quality guidelines and management principles are included in *Annex III* (Waste Disposal and Waste Management) of the *Protocol on Environmental Protection to the Antarctic Treaty*, which requires countries to preserve the environment for future generations. The rules in this document state that wastewater can be discharged directly into Antarctic marine waters (Article 5, Annex III), only if proper dilution and rapid dispersion are ensured. It has been proven that the Antarctic environment creates good conditions for dispersion of wastewater at the discharge points, which is caused by local hydrodynamic conditions, especially tides [71].

The verification of the third detailed hypothesis is presented in the article: **Szopińska M., Łuczkiewicz A., Jankowska K., Fudala-Książek S., Potapowicz J., Kalinowska A., Bialik R.J., Chmiel S., Polkowska Ż., First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica), *Sci. Total Environ.*, 789 (2021) 147912 [publication VII]**. Samples of wastewater and water after discharge into Admiralty Bay were collected at different time intervals during research expeditions in 2017 and 2019 and analysed. The research included 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. In addition, principal component analysis (PCA) was performed to observe potential correlations and (due to the data's suitability for the purpose) to contribute towards a preliminary risk assessment. The simplified risk assessment was made by comparing the obtained results against no-observed-effect concentrations (NOECs) for selected Antarctic bioindicators.

Based on the measurements taken and the results obtained, it was confirmed that the proposed set of contaminants can be determined by simple analytical procedures (including spectrophotometric methods). In addition, they may be useful for routine

analysis in Antarctica to monitor compliance with environmental regulations. This is particularly true for parameters such as SC, SA and SNI surfactants, which we confirmed are markers of human activity in Antarctica. Moreover, based on the results of chemical analyses, no wastewater contamination was detected in seawater after one day due to natural processes – except for the presence of anionic surfactants and Zn. Comparing the results against the assumptions of the Protocol requirements (Annex III, Article 5), Arctowski Station's wastewater management was proven to comply with the requirements set out in this document and that the receiving marine environment provided assimilative capacity, suitable dilution and rapid dispersal conditions. Based on the determination of chemical compounds by simple analytical methods, it can be tentatively stated that this method of wastewater management has little effect on Antarctic ecosystems. However, this is not conclusively confirmed, as the scope of knowledge should be expanded to include analyses of other groups of chemical pollutants as well as bottom sediments in Admiralty Bay.

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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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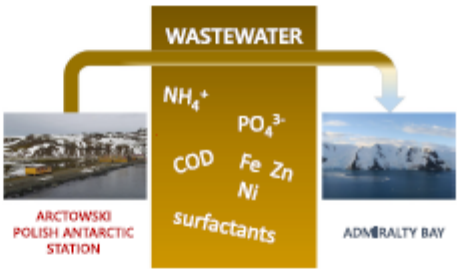
HIGHLIGHTS

- Arctowski Station wastewater management met the Madrid Protocol requirements.
- Anionic surfactants and Zn were noted in marine water 96 h after wastewater discharge.
- The sum of surfactants may be used as markers of human activity in Antarctica.
- No observed effect concentrations on bioindicators may be used for risk assessment.
- Suitable wastewater treatment systems in Antarctica is needed.

GRAPHICAL ABSTRACT



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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.

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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; Kumar Bharti 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; Stark et al., 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 (de C. Martins et al., 2005; Martins et al., 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 (de C. Martins et al., 2005; Martins et al., 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 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 (de C. Martins et al., 2005, Martins et al., 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 (de C. Martins et al., 2005; Martins et al., 2002; Stark et al., 2016; Stark et al., 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

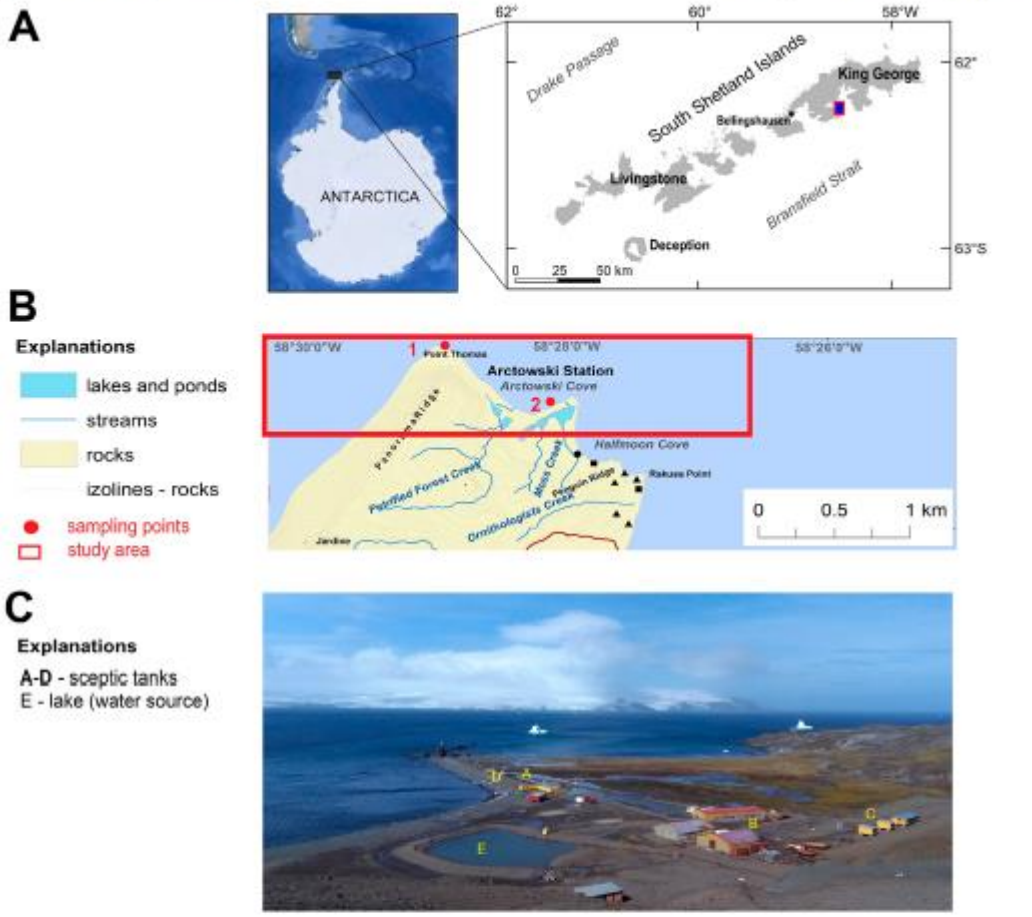


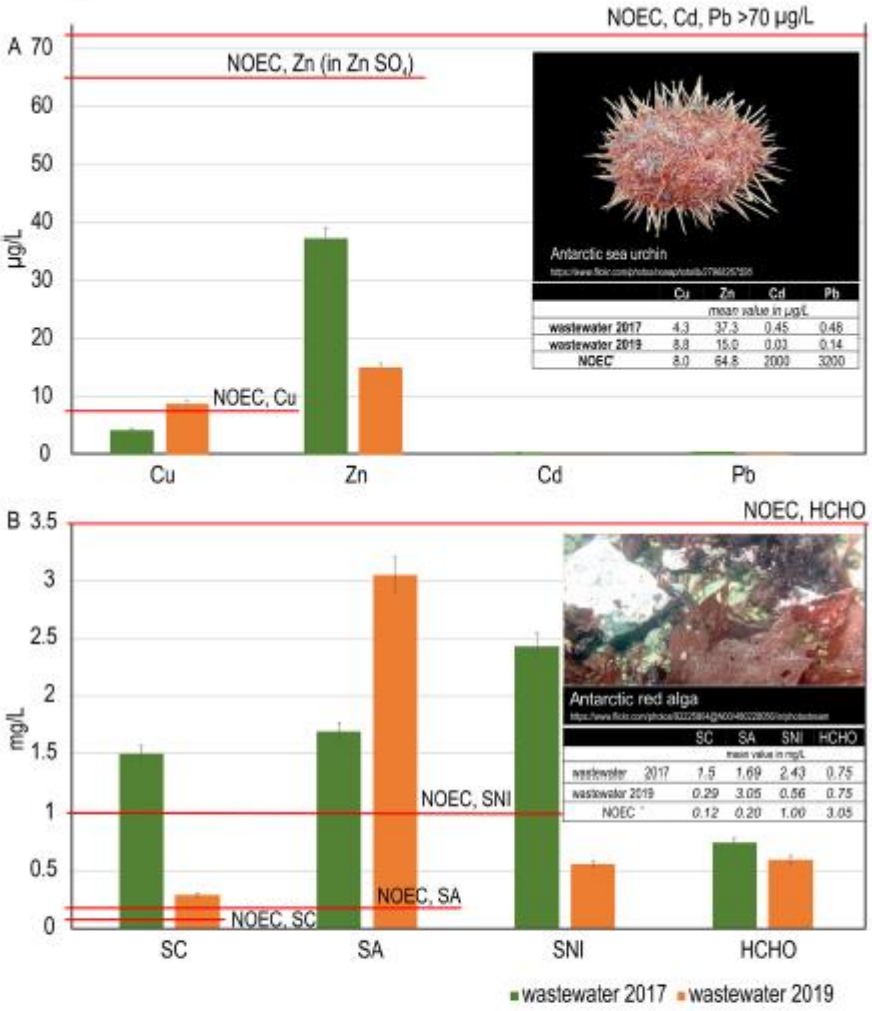
Fig. 1. Location of the study area: A) location of King George Island in relation to Antarctica; B) location of Arctowski Station and sampling points; and C) location of Arctowski Station facilities and septic tanks.
Panels A and B are adapted from Szopińska et al. (2018)).

dispersal" of discharged wastewater. Nonetheless, to date, no research concerning the possible contamination of local marine ecosystems has been conducted.

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 1 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



	Cu	Zn	Cd	Pb
	mean value in µg/L			
wastewater 2017	4.3	37.3	0.45	0.48
wastewater 2019	8.8	15.0	0.03	0.14
NOEC*	8.0	64.8	2000	3200

	SC	SA	SNI	HCHO
	mean value in mg/L			
wastewater 2017	1.5	1.69	2.43	0.75
wastewater 2019	0.29	3.05	0.56	0.75
NOEC*	0.12	0.20	1.00	3.05

Fig. 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.* (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Discrimination. A multi-element ICP-MS standards mix 10 mg L^{-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 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 2 h. 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 and 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. 3A,C) and without (Fig. 3B,D). For this analysis the redox parameter has been excluded. In addition, in the case of data without raw wastewater (Fig. 3B,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. 3A), 96% (Fig. 3B), 99% (Fig. 3C) and 99% (Fig. 3D) of the variance, respectively. For the first case (Fig. 3A), 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. 3C) 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. 3D), in which some of the variables were omitted.

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

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

STATION NAME (ownership)	YEAR	TSS	COD_{total} ($COD_{filtrated}$)	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)

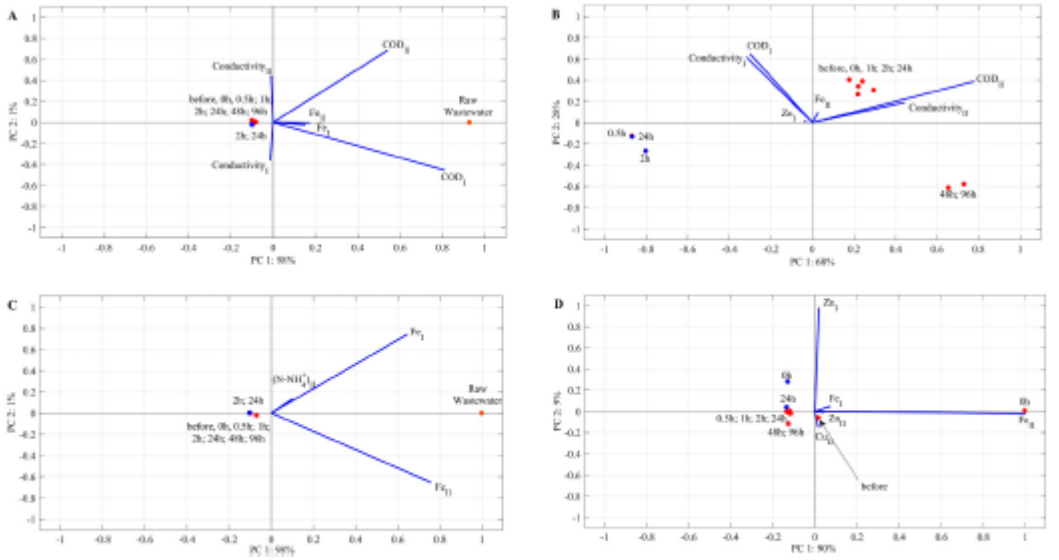


Fig. 3. PCA biplots for various data sets. Projection of environmental variables and cases (sampling points) on the plane of two principal components: A. Entire data set for recipient water and raw wastewater analysis (excluding redox parameter); B. Entire data set for recipient water C. Reduced data 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. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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.

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 ≥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. 3C, 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; Tjandraatmadja 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 *qacE* 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 µg/L^{-1}, and Zn: 56 ± 31 and 195 ± 44 µg/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 micropollution 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.

4.2. 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 processes e.g. activated carbon technologies (Kosek et al., 2020) have been applied consecutively in the context of pharmaceutical and other organic micropollution 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 micropollution contamination. According to the available survey, in the majority of Antarctic stations, there is a lack of wastewater treatment. 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 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 1 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.

CRediT authorship contribution statement

Małgorzata Szopińska: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition. **Aneta Łuczkiewicz:** Conceptualization, Writing – review & editing. **Katarzyna Jankowska:** Conceptualization, Investigation. **Sylwia Fudala-Książek:** Visualization, Writing – review & editing. **Joanna Potapowicz:** Validation, Writing – review & editing. **Agnieszka Kalinowska:** Writing – review & editing. **Robert Józef Bialik:** Visualization, Formal analysis. **Stanisław Chmiel:** Investigation. **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 Material consists of: S1. Additional information regarding the influence of wastewater discharge in Admiralty Bay, and S2. Detailed information regarding the applied chemical methods. Supplementary data to this article can be found online at doi:https://doi.org/10.1016/j.scitotenv.2021.147912.

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The continuation of the third hypothesis verification is presented in the paper **Szopińska M., Potapowicz J., Jankowska K., Łuczkiewicz A., Svahn O., Björklund E., Nannou C., Lambropoulou D., Polkowska Ż, Pharmaceuticals and other contaminants of emerging concern in Admiralty Bay as a result of untreated wastewater discharge: Status and possible environmental consequences, *Sci. Total Environ.*, 835 (2022) 155400 [publication VIII]**. The article presents the research results that 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). In addition, the environmental risk of the detected substances and genes to Antarctic aquatic ecosystems was assessed.

Chemical analyses allowed us to identify the presence of 34 PPCPs and other ECs from among the more than 170 substances analysed in the water and wastewater samples collected in the surroundings of the Arctowski Station (western shore of Admiralty Bay). Samples were taken during two field campaigns in 2017 and 2019. Water from the bay was collected at time intervals, starting from the moment of wastewater discharge. On the basis of the results obtained, it was concluded that many of these substances that are not neutralised or are difficult to neutralise are excreted into the wastewater and ultimately reach the aquatic environment after discharge. As a result of the analyses, the presence of antibiotic resistance genes (ARGs) was found in the study area, which may raise concerns. The obtained data on resistome changes in polar regions significantly improves the capacity to recognise and solve threats to Antarctic fauna and flora.

Therefore, an important element is the control of the use of drugs in polar stations, e.g. in the form of a centralised record of the medication prescribed and consumed in situ. Additionally, the emission of harmful substances into the environment could be reduced by using more environmentally friendly substitutes for both pharmaceuticals and personal care products (limiting consumption at the source). In addition to constant monitoring of PPCPs and other ECs in Antarctica concentrations, it is also recommended to perform more detailed analysis of the antimicrobial resistance phenomenon.

As a result of the conducted chemical analyses, the presence of many anthropogenic pollutants was found in Admiralty Bay. Moreover, the concentrations of some contaminants exceeded the values that pose a threat to the representatives of the Antarctic ecosystem. It can therefore be concluded that untreated wastewater discharge into the Admiralty Bay constitutes a threat to the marine Antarctic environment. Because some of the chemical contaminants are persistent in the environment, preventive and mitigating solutions were proposed to minimise their negative effects.

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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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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 ng·L^{-1}), diclofenac (747 ng·L^{-1}), ketoconazole (760 ng·L^{-1}), ibuprofen (477 ng·L^{-1}) and acetaminophen (332 ng·L^{-1}). Moreover, the concentrations of benzotriazole (6340 ng·L^{-1}) and caffeine (3310 ng·L^{-1}) 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 centralized 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 °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^3 (Szopińska et al., 2021).

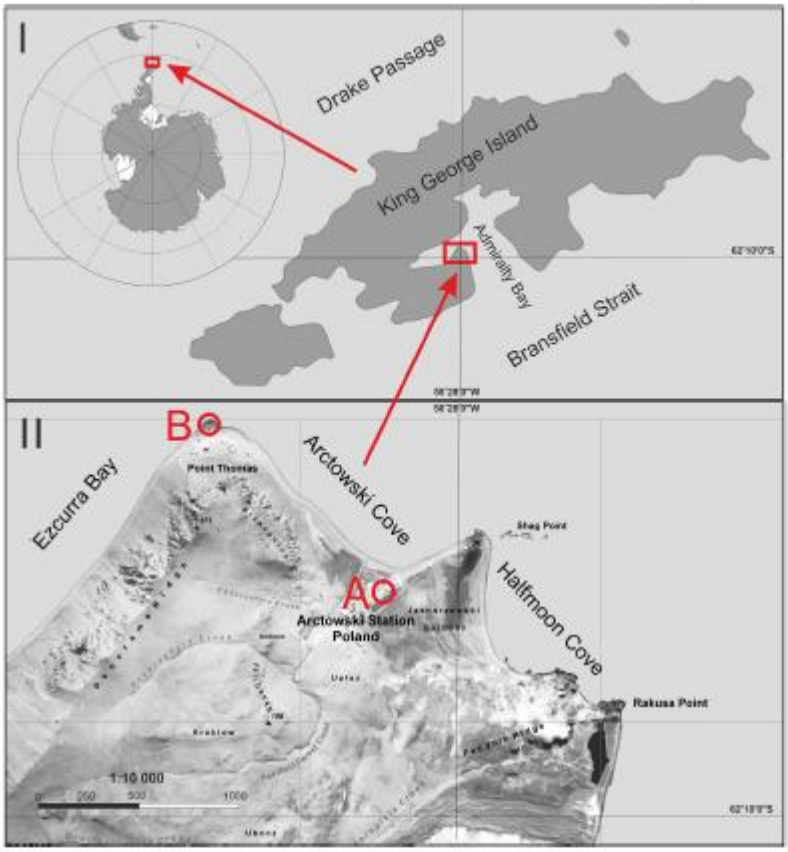

Fig. 1. Location of sampling points: (I) in the context of Antarctic continent and (II) considering their geographic location at the western shore of Admiralty Bay (Arctowski Station, King George Island) presented in a fragment of the orthophotomap by Pudełko (2007).

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 °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 (Na_2EDTA), 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 $mg\,L^{-1}$) were prepared in methanol (LC–MS grade) and stored in darkness at -20 °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 mg, 6 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 °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 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-μm 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 μm).

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 ± 0.1 min, (b) the mass error of the quantification peak should be not more than ± 5 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 L) were filtered through polycarbonate membrane filters (0.22 μm) and stored at -20 °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 μL containing: 10 μL of Real Time 2xRT-PCR Mix SYBRA (A&A Biotechnology), 0.4 μL of respective primers (stock concentration 10 μM), 1 μL of extracted DNA template (10 ngμl^{-1}) and 8.2 μL of nuclease-free water. The qPCR cycling programme consisted of 3 min of initial denaturation at 95 °C, followed by 40 cycles of: denaturation at 95 °C for 15 s, followed by primer annealing at 60 °C for 30 s (58 °C for bacterial 16S rRNA genes) and primer elongation at 72 °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):

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

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:

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

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^{-1}), naproxen (NAP; 662–2653 ngL^{-1}) and ketoconazole (KCZ; 760 ngL^{-1}), as well as for benzotriazole (BTA, 72–6340 ngL^{-1}), 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^{-1}) together with ibuprofen (IBP, 477 ngL^{-1}) and caffeine (CAF, 3310 ngL^{-1}) (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^{-1}), DIC (15.09 μgL^{-1}) and IBP (10.05 μgL^{-1}), and for the stimulant CAF (71.33 μgL^{-1}). 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 muscolo-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 (Evanson, 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^{-1}), and low amounts in seawater (4.65 ngL^{-1}) (Table 2). In comparison to other studies in the US and Europe, it was quantified in influent wastewater at 2–43 mgL^{-1} and in effluent wastewater at 0.025–4.3 μgL^{-1} (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).

PPCPs and other EC concentrations in ngL^{-1}

PPCP or EC type	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 stabilizers for plastics	Plasticizer
Sample name/substance name	*Trimethoprim*	*Carbamazepine*	*Metoprolol*	*Diclofenac*	*Naproxen*	*Losartan*	*Oxazepam*	*Ketoconazole*	*Venlafaxine*	*Imidacloprid*	*Benzotriazole*	*Bisphenol A*
Substance abbreviation	*TRI*	*CBZ*	*MET*	*DIC*	*NAP*	*LST*	*OZ*	*KCZ*	*VEN*	*IMD*	*BTA*	*BPA*
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
2017												
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_1h	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
2019												
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
Blanks	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	Antibiotics			Analgetics and muscle relaxants	Anticonvulsants	Antihistamines	Anaesthetics	Antidiarrhoeals	Antidiabetics	Beta-blockers		β2 adrenergic receptor agonist
Substance name	Clindamycin	Trimethoprim	Isoniazid	Acetaminophen	Carbamazepine	Cetirizine	Lidocaine	Loperamide	Metformin	Atenolol	Carvedilol	Salbutamol
Substance abbreviation	CLI	TRI	INH	APAP	CBZ	CET	LD	LO	MTN	ATEN	CAR	SBS
MQL (wastewater/seawater)	50/10	0.01/0.01	25/50	1.2/1.3	0.7/0.7	3/14	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	132	<MQL	<MQL	<MQL	13.5	2.58	<MQL	NF	<MQL
Seawater_0h	NF	2.98	NF	4.65	NF	NF	NF	NF	NF	NF	<MQL	NF
Seawater_1h	NF	NF	NF	<MQL	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_2h	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_24h	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_48h	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_96h	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF

PPCP type	Cardiovascular agent	Insect repellent	UVA/UVB filters		Lipid regulators	Nonsteroidal anti-inflammatory drugs			Stimulant	Boosting supplement	
Sample name/substance name	Methyldopa	N,N-Diethyl-meta-toluamide	para-aminobenzoic acid	Benzophenone 1	Atorvastatin	Ibuprofen	Nimesulide	Ketoprofen	Diclofenac	Caffeine	Caffeic Acid
Substance abbreviation	MDOP	DEET	PABA	BP-1	AT	IBP	NIM	KET	DIC	CAF	CA
MQL (wastewater/seawater)	15/15	0.1/0.2	6.8/16.7	0.4/1.3	1.7/45.5	50/50	10/0.2	0.5/0.5	5/5.1	0.5/0.17	10/1.4
Sample name											
wastewater	7.86	6.21	17.7	4.48	7.67	477	NF	14.61	19.4	1310	<MQL
Seawater_0h	NF	<MQL	NF	<MQL	NF	<MQL	17.1	4.47	<MQL	49.9	NF
Seawater_1h	NF	<MQL	NF	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_2h	NF	<MQL	NF	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_24h	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_48h	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
Seawater_96h	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF

Abbreviations: NF – not found (<MDL); MDL – method detection limit; MQL – method quantification limit.

in water (Zadaliasghar 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^{-1}) 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^{-1}, while the total number of offspring per female decreased at 3000 ngL^{-1}. 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^{-1}.

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^{-1} in the dissolved phase and 5 ngL^{-1} in total water analysis; (2) clindamycin (CLI), which is a bactericidal agent, was found in concentrations <50 ngL^{-1}; and (3) isoniazide (INH) is used for treatment of tuberculosis and was found in concentrations <25 ngL^{-1}. 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^{-1}, while benzophenone 1 (BP-1) was quantified at 4.48 ngL^{-1}. 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^{-1}; 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^{-1}). 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^{-1} for BTA in wastewater and 71.0–98.3 ngL^{-1} 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^{-1} in fresh water (streams) and 172 ngL^{-1} in untreated wastewater for BTA and <0.12–18.74 ngL^{-1} in

fresh water (streams) and <0.12 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 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 (4.2×10^{-2} and 9.6×10^{-6} 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 (2.1×10^{-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 (Tenaillon et al., 2010); thus, a large number of them might be realised to wastewater and then (depending on wastewater treatment efficiency) to

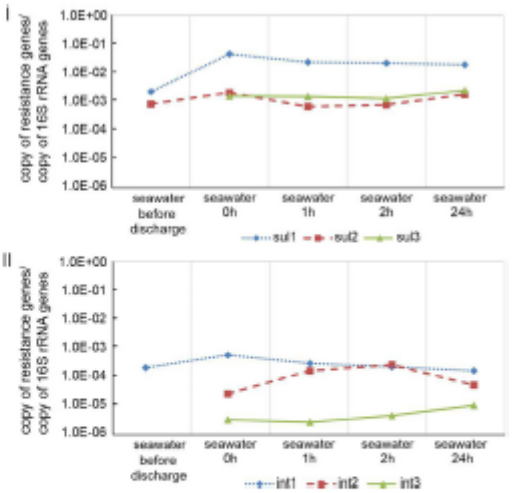

Fig. 2. Copies of resistance genes: (I) sul 1–3 (II) int 1–3, normalised to the number of Bacterial 16S rRNA genes prior to, during and at a certain time after the discharge of wastewater to Admiralty Bay.

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 μgL^{-1} (US legislation) or 10 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 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 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 [ng L^{-1}]	Max detected concentration in marine water [ng L^{-1}]	Marine organisms name (parent category) if available	PNEC [ng L^{-1}]	Risk Quotients [wastewater] value/risk	Risk Quotients [marine water] value/risk	References
Pharmaceuticals								
Analgesics and muscle relaxants	Acetaminophen	332	<10	Pinnphales 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)
Personal Care Products								
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
Other ECs								
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 anthopopressure 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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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 Łuczkiewicz:** 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

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8. Summary

Due to its geographical isolation and extremely unfavourable weather conditions, Antarctica remained relatively free of any pollution for a very long time, making it an excellent place to study environmental changes. For this reason, the area around the South Pole has become a site for numerous studies on air quality, soil, cryosphere and aquatic environment. The constantly, dynamically developing urbanisation of highly industrialised areas and the related long-range transport of thousands of toxic compounds, as well as growing Antarctic tourism and the construction of scientific and research stations, have increased the concentration of chemical pollutants.

As part of this study, samples of surface waters, sediments and snow from several locations on ASMA 1 (King George Island) at different distances from the Polish Antarctic Station and Carlini Station (Argentina) were analysed. This made it possible to determine the impact of global and local human activity on the amount of pollution in Antarctic ecosystems. Based on the analysis of the test results, the **presence of chemical pollutants in the tested samples was confirmed** and it was shown that **snow and ice-cover meltwaters may affect the chemistry of Antarctic waters and sediments**. An important phenomenon that may affect the re-release of accumulated compounds into the environment is **the increase in global air temperature**. It intensifies the degradation of features of the cryosphere, including permafrost, melting glaciers and snow cover, and thus also contributes to the re-emission of chemical compounds accumulated there. It has also been proven that **long-range atmospheric transport** of pollutants and their deposition in areas of little anthropogenic activity can significantly modify the chemical composition of various elements of the environment.

However, analysis of the data determined that wastewater discharge on the western coast of Admiralty Bay is **a source of organic micropollutants in seawater**. The concentrations of some pollutants exceeded the values that affect the life cycle of representatives of the Antarctic ecosystem. The research period being only two years, we could not state to what extent long-term exposure to low concentrations of PPCPs and other ECs is harmful to fauna and flora. Though the risk of this harm should not be underestimated, longitudinal studies would be required to assess it.

The results of the analyses included in doctoral dissertation confirm the following:

(1) There was variation in the values of physicochemical parameters of creeks and lakes depending on feeding source in the area of the western coast of Admiralty Bay.

(2) There are water–sediments–snow interactions that influence the transport and distribution of pollutants in the study area and correlations between these elements of the environments result in changes in chemistry of each of matrix.

(3) Untreated wastewater discharge into the Admiralty Bay constitutes a threat to the marine Antarctic environment.

The analysis of the available information shows that human activity on a local and global scale is leading to degradation of Antarctic ecosystems. The main direction of contemporary polar research on pollution should be to determine Antarctic fauna and flora's responses and levels of tolerance to chemical anthropogenic disturbances in the environment and to mitigate their negative effects. Moreover, it is worth paying attention to changes in legislation and intensification of programmes aimed at verifying the degree of human impact in other areas.

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10. Research achievements

Publications:

1. **Joanna Potapowicz**, Danuta Szumińska, Małgorzata Szopińska, Żaneta Polkowska, The influence of global climate change on the environmental fate of anthropogenic pollution released from the permafrost. Part I. Case study of Antarctica, *Sci. Total Environ.*, 651, 1534-1548, 2019, doi 10.1016/j.scitotenv.2018.09.168, (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.
2. **Joanna Potapowicz**, Dimitra Lambropoulou, Christina Nannou, Krystyna Kozioł, Żaneta Polkowska, Occurrences, sources, and transport of organochlorine pesticides in the aquatic environment of Antarctica, *Sci. Total Environ.*, 725, 139475, 2020, doi 10.1016/j.scitotenv.2020.139475 (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.
3. **Joanna Potapowicz**, Danuta Szumińska, Małgorzata Szopińska, Sebastian Czapiewski, Żaneta Polkowska, , Electrical conductivity and pH in surface water as tool for identification of chemical diversity, *Ecol. Chem. Eng., S*, 27, 95-111, 2020, doi 10.2478/eces-2020-0006, (IF: 1.545; 5-Year IF: 1.504; 40 pt), Q3.
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7. Małgorzata Szopińska, Aneta Łuczkiewicz, Katarzyna Jankowska, Sylwia Fudala-Książek, **Joanna Potapowicz**, Agnieszka Kalinowska, Robert Józef Bialik, Stanisław Chmiel, Żaneta Polkowska, First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica), *Sci. Total Environ.*, 789, 147912, 2021, doi 10.1016/j.scitotenv.2021.147912, (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.
8. Małgorzata Szopińska, **Joanna Potapowicz**, Katarzyna Jankowska, Aneta Łuczkiewicz, Ola Svahn, Erland Björklund, Christina Nannou, Dimitra Lambropoulou, Żaneta Polkowska, Pharmaceuticals and other contaminants of emerging concern in Admiralty Bay as a result of untreated wastewater discharge: Status and possible environmental consequences, *Sci. Total Environ.*, 835, 155400, 2022, doi 10.1016/j.scitotenv.2022.155400, (IF: 7.963; 5-Year IF: 7.842; 200 pt), Q1.
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1. Klaudia Kosek, Małgorzata Szopińska, **Joanna Potapowicz**, Horyzontem II za koło polarne – arktyczna wyprawa polarna naukowców z Politechniki Gdańskiej, *Pismo PG*, 39–41, Gdańsk 2020, ISSN: 1429-4494.

Conferences:

1. Małgorzata Szopińska, **Joanna Potapowicz**, Erwin Rosenberg, Żaneta Polkowska, *Application of GC-MS/MS for analysis of PAHs and PCBs in polar environmental samples*, ISSS 2017 – 23rd International Symposium on Separation Sciences, Vienna 19–22.09.2017 (poster).

2. Małgorzata Szopińska, Danuta Szumińska, Robert Bialik, **Joanna Potapowicz**, Żaneta Polkowska, *Markers of anthropogenic activities in fresh waters at periglacial environments (Western Shore of Admiralty Bay, King George Island, Antarctica),*

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3. **Joanna Potapowicz**, Małgorzata Szopińska, Danuta Szumińska, Stanisław Chmiel, Robert Józef Bialik, Żaneta Polkowska, *Selected chemical determinants of human activity in land-surface and shallow aquatic sediments at cold environment (King George Island, South Shetland Island, Antarctica)*, XXXVII Sympozjum Polarne Polar Change – Global Change, Poznań 7–10.06.2018 (poster).
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5. Małgorzata Szopińska, Danuta Szumińska, **Joanna Potapowicz**, Robert Józef Bialik, Żaneta Polkowska, *Examination of fresh water chemistry at Lions Rump headland (Maritime Antarctica, King George Island) – preliminary results*, XXXVII Sympozjum Polarne Polar Change - Global Change, Poznań 7–10.06.2018 (poster).
6. Małgorzata Szopińska, Aneta Łuczkiewicz, Katarzyna Jankowska, Sylwia Fudala-Książek, **Joanna Potapowicz**, Klaudia Kosek, Żaneta Polkowska, *Problems of micropollutants introduced with wastewater into the Admiralty Bay (Maritime Antarctica)*, Mikrozanieczyszczenia w środowisku człowieka, Częstochowa 4–6.09.2019 (presentation).
7. **Joanna Potapowicz**, Małgorzata Szopińska, Danuta Szumińska, Robert Józef Bialik, Żaneta Polkowska, *Occurrence and spatial distribution of polycyclic aromatic hydrocarbons in sediments and surface water on the western shore of the Admiralty Bay (King George Island, Maritime Antarctica)*, 38th International Polar Symposium "Environmental changes in polar regions: new problems – new solutions" Toruń, 18–20.11.2021 (poster).
8. Klaudia Kosek, Marek Ruman, **Joanna Potapowicz**, Sebastian Czapiewski, Aneta Łuczkiewicz, Żaneta Polkowska, *Revelva catchment: chemical characteristics and changes in the concentration levels of selected pollutants over two summer seasons, southernwestern Svalbard*, 38th International Polar Symposium "Environmental changes in polar regions: new problems – new solutions" Toruń, 18–20.11.2021 (poster).

9. Małgorzata Szopińska, Danuta Szumińska, **Joanna Potapowicz**, Robert Józef Bialik, Stanisław Chmiel, Żaneta Polkowska, *Heavy metals content in fresh water samples at Lions Rump headland (Maritime Antarctica, King George Island)*, 38th International Polar Symposium "Environmental changes in polar regions: new problems – new solutions" Toruń, 18–20.11.2021 (poster).
10. Danuta Szumińska, **Joanna Potapowicz**, Małgorzata Szopińska, Sebastian Czapiewski, Żaneta Polkowska, *Distribution of Persistent Organic Pollutants (POPs) in Antarctic biotic and abiotic environment (South Shetland Islands)*, 38th International Polar Symposium "Environmental changes in polar regions: new problems – new solutions" Toruń, 18–20.11.2021 (poster).

Internships and expeditions:

1. Participation in the polar expedition to the Polish Polar Station Hornsund S. Siedlecki on Spitsbergen as part of the grant project "Preludium 13", No. 2017/25/N/NZ9/01506, entitled "Determination of nutrients that are the basic factor enabling the growth of bacteriocenosis in the Arctic river basin of south-west Spitsbergen", led by Klaudia Kosek, PhD. 07–28.09.2018.
2. Internship in the laboratory of the Department of Hydrology and Climatology at the Faculty of Earth Sciences and Spatial Management of the Maria Curie-Skłodowska University in Lublin, 12–18.11.2018.
3. Participation in the polar expedition to the Polish Antarctic Station H. Arctowski on King George Island (Antarctica) under project No. POWR.03.02.00-IP.08-00-DOK/16 entitled "Development of an interdisciplinary PhD studies with an international dimension", 17.01–17.04.2019.
4. Internship in the Environmental Pollution Control Laboratory at Aristotle University of Thessaloniki (Department of Chemistry) under the project No. POWR.03.02.00-IP.08-00-DOK/16 entitled "Development of an interdisciplinary PhD studies with an international dimension", 02.07–30.09.2019.
5. Participation in the polar expedition to the Polish Polar Station Hornsund S. Siedlecki on Spitsbergen as part of the grant project "Preludium 13", No. 2017/25/N/NZ9/01506, entitled "Determination of nutrients that are the basic factor

enabling the growth of bacteriocenosis in the Arctic river basin of south-west Spitsbergen, PhD. 24.08–15.09.2020.

6. Participation in the polar expedition as part of a grant project financed by the National Science Centre (2020/37/N/ST10/02199); King George Island, Polish Antarctic Station; "Determination and characterization of pollutants release as a result of climate change from glaciers and snow melting in Antarctica", 15.11.2021–14.02.2022.

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Courses, trainings, workshops:

- "*Problems of water quality in coastal areas*", organisers: Coastal Landscape Park, Gdańsk University of Technology, University of Silesia, Władysławowo, 2–4.03.2018.
- *"The latest technological solutions for analytical chemistry"*, Shim-pol, Gdańsk, 24.10.2018.
- "*Water quality in the context of local and global dispersion of pollutants*", organisers: Coastal Landscape Park, Gdańsk University of Technology, University of Silesia, Władysławowo, 8–10.03.2019.
- training in rope belaying, avalanche auto-rescue and ice-crevice auto-rescue (winter tourism), Zakopane, near Eye of the Sea and Black Lake below Mount Rysy, 1–3.03.2020.
- *"A new approach to personal data protection after the entry of GDPR"*, Uniseco Sp z o.o., Gdańsk, 13.04.2021.
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Joanna Potapowicz, Danuta Szumińska, Małgorzata Szopińska, Robert Józef Bialik, Katarzyna Machowiak, **Stanisław Chmiel**, Żaneta Polkowska, *Seashore sediment and water chemistry at the Admirality Bay (King George Island, Maritime Antractica) – geochemical analysis and correlations*, Mar. Pollut. Bull., 152, 110888, 2020, doi 10.1016/j.marpolbul.2020.110888 (5-Year IF: 5.907), Q1.	Methodology, Investigation, Resources, Writing - Review & Editing
Małgorzata Szopińska, Aneta Łuczkiewicz, Katarzyna Jankowska, Sylwia Fudala-Książek, Joanna Potapowicz, Agnieszka Kalinowska, Robert Józef Bialik, **Stanisław Chmiel**, Żaneta Polkowska, *First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica)*, Sci. Total Environ., 789, 147912, 2021, doi 10.1016/j.scitotenv.2021.147912, (5-Year IF: 7.842), Q1.	Investigation

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Danuta Szumińska, Joanna Potapowicz, Małgorzata Szopińska, **Sebastian Czapiewski**, Ulrike Falk, Marcin Frankowski, Żaneta Polkowska, *Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 2: Organic and inorganic chemicals in snow cover at the Warszawa Icefield*, Sci. Total Environ., 796, 149054, 2021, doi 10.1016/j.scitotenv.2021.149054, (5-Year IF: 7.842), Q1.	Software, Formal analysis, Writing – original draft, Writing – review & editing, Visualization

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Małgorzata Szopińska, Aneta Łuczkiewicz, Katarzyna Jankowska, **Sylwia Fudala-Książek**, Joanna Potapowicz, Agnieszka Kalinowska, Robert Józef Bialik, Stanisław Chmiel, Żaneta Polkowska, *First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica)*, Sci. Total Environ., 789, 147912, 2021, doi 10.1016/j.scitotenv.2021.147912, (5-Year IF: 7.842), Q1.	Visualization, Writing – review & editing

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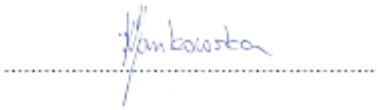
Malgorzata Szopińska, Joanna Potapowicz, **Katarzyna Jankowska**, Aneta Łuczkiewicz, Ola Svahn, Erland Björklund, Christina Nannou, Dimitra Lambropoulou, Żaneta Polkowska, *Pharmaceuticals and other contaminants of emerging concern in Admiralty Bay as a result of untreated wastewater discharge: Status and possible environmental consequences*, Sci. Total Environ., 155400, 2022, doi 10.1016/j.scitotenv.2022.155400, (5-Year IF: 7.842), Q1.	Conceptualization, Visualization



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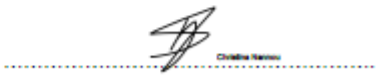

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Danuta Szumińska, **Joanna Potapowicz**, Małgorzata Szopińska, Sebastian Czapiewski, Ulrike Falk, Marcin Frankowski, Żaneta Polkowska, *Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 2: Organic and inorganic chemicals in snow cover at the Warszawa Icefield*, Sci. Total Environ., 796,	Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Writing – review & editing, Visualization, Supervision, Project

149054, 2021, doi 10.1016/j.scitotenv.2021.149054, (5-Year IF: 7.842), Q1.	administration
Małgorzata Szopińska, Aneta Łuczkiewicz, Katarzyna Jankowska, Sylwia Fudala-Książek, **Joanna Potapowicz**, Agnieszka Kalinowska, Robert Józef Bialik, Stanisław Chmiel, Żaneta Polkowska, *First evaluation of wastewater discharge influence on marine water contamination in the vicinity of Arctowski Station (Maritime Antarctica)*, Sci. Total Environ., 789, 147912, 2021, doi 10.1016/j.scitotenv.2021.147912, (5-Year IF: 7.842), Q1.	Validation, Writing – review & editing
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Joanna Potapowicz, **Małgorzata Szopińska**, Danuta Szumińska, Robert Józef Bialik, Żaneta Polkowska, *Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 1: Sediment and water analysis for PAH sources evaluation in the vicinity of Arctowski station*, Chemosphere, 288, 132637, 2022, doi 10.1016/j.chemosphere.2021.132637, (5-Year IF: 6.956), Q1.	Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration
Danuta Szumińska, Joanna Potapowicz, **Małgorzata Szopińska**, Sebastian Czapiewski, Ulrike Falk, Marcin Frankowski, Żaneta Polkowska, *Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 2: Organic and inorganic chemicals in snow cover at the Warszawa Icefield*, Sci. Total Environ., 796, 149054, 2021, doi 10.1016/j.scitotenv.2021.149054, (5-Year IF: 7.842), Q1.	Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing
Małgorzata Szopińska, Aneta Łuczkiewicz, Katarzyna Jankowska, Sylwia Fudala-Książek, Joanna Potapowicz, Agnieszka Kalinowska, Robert Józef Bialik, Stanisław Chmiel, Żaneta Polkowska, *First evaluation of wastewater*	Conceptualization, Methodology, Investigation, Visualization, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition

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Statement of contribution

I have contribute to the publication that constitutes a part of PhD dissertation in the following way:

Publication	Contribution to the article
Joanna Potapowicz, **Danuta Szumińska**, Małgorzata Szopińska, Żaneta Polkowska, *The influence of global climate change on the environmental fate of anthropogenic pollution released from the permafrost. Part I. Case study of Antarctica*, Sci. Total Environ., 651, 1534-1548, 2019, doi 10.1016/j.scitotenv.2018.09.168, (5-Year IF: 7.842), Q1.	Validation, Resources, Writing - Review & Editing, Visualization, Project administration
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