



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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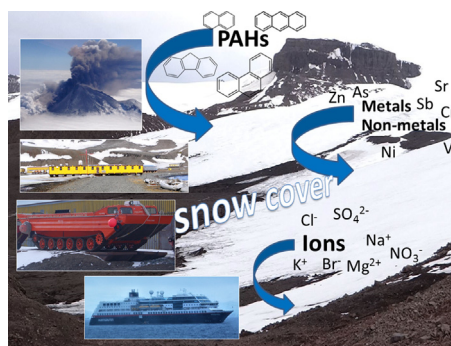
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HIGHLIGHTS

- 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 NO_x (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 there 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 km²), 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 (ASP 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 (Pętllicki et al., 2017; Pudełko et al., 2018; Sziło and

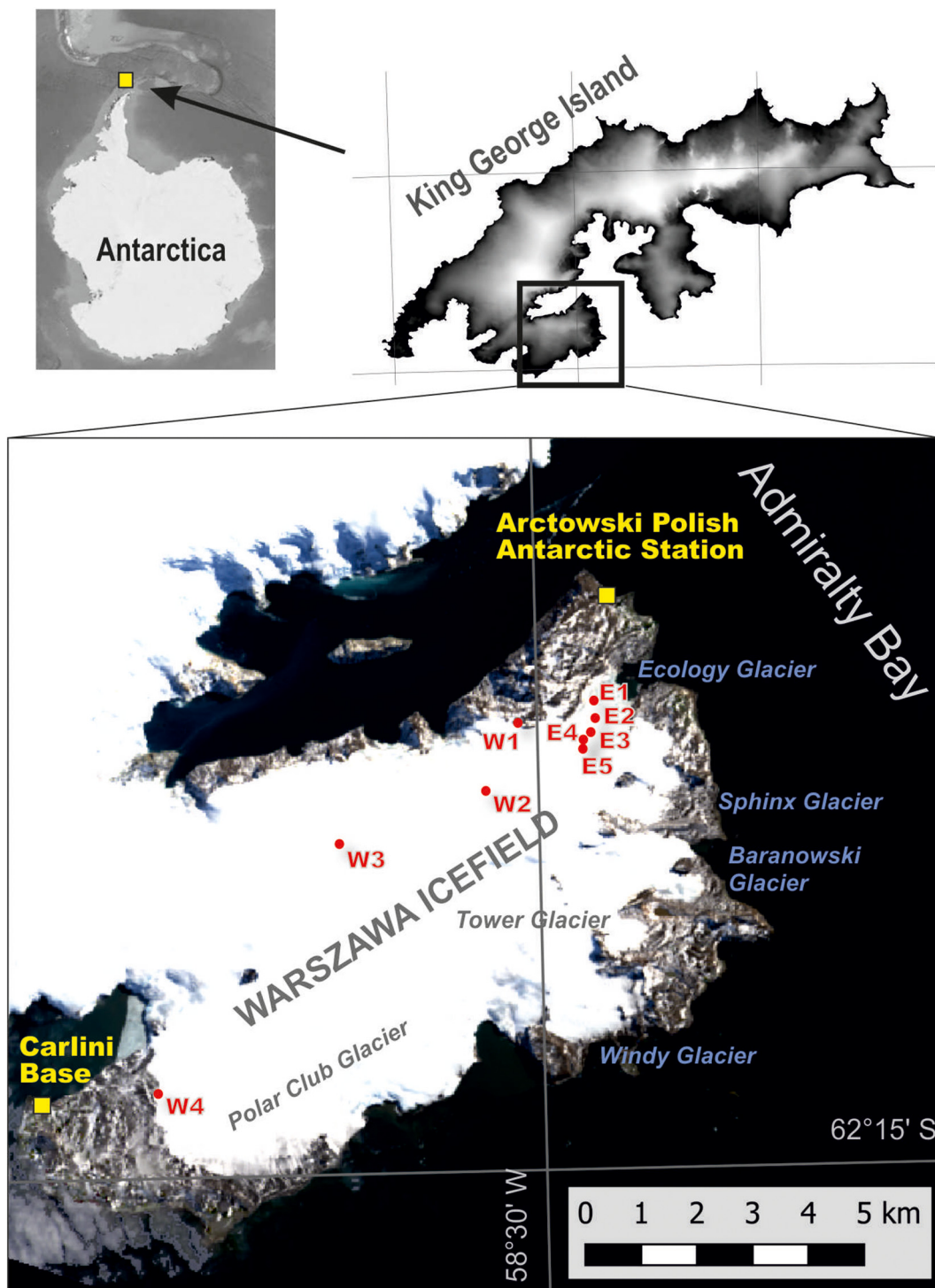


Fig. 1. Study area and sampling points location (prepared based on Landsat Image LC08_L1GT_217103_20180309_20180320_01_T2 – Level 2, obtained from www.usgs.gov, Google Earth application) (Google Earth, 2018; USGS.gov, 2018, p. 08).

Bialik, 2018). According to Pudełko et al. (2018), ASPA 128 lost around 30% (6.1 km²) 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 (Pętllicki et al., 2017; Sziło and Bialik, 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 (Pętllicki 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: $\text{nssSO}_4^{2-} = \text{SO}_4^{2-} - (\text{SO}_4^{2-} / \text{Cl}^-)_{\text{seawater}} * \text{Cl}^-$. The $(\text{SO}_4^{2-} / \text{Cl}^-)_{\text{seawater}}$ 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 m a.s.l.	Na^+ mg/L	K^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	Cl^- mg/L	NO_3^- mg/L	SO_4^{2-} mg/L	TOC 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.

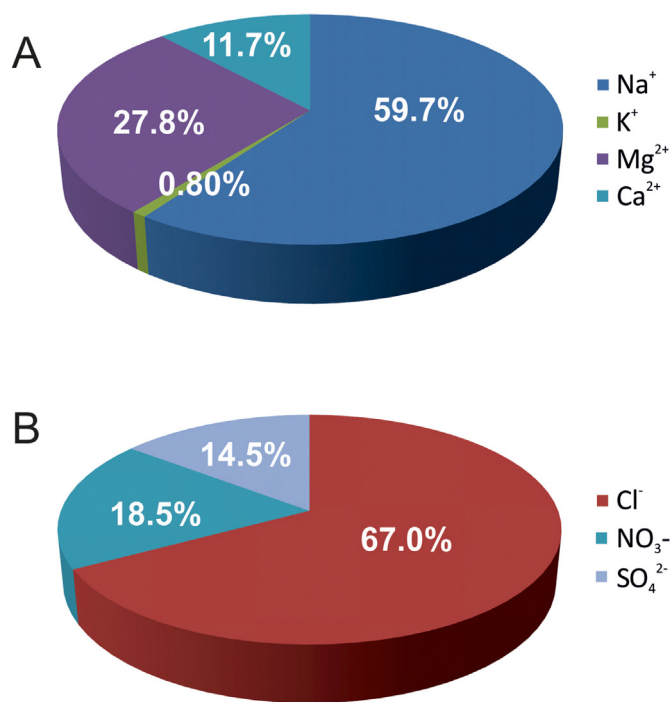


Fig. 2. Percentage of individual ions in the total of: A. cations; B. anions.

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.

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	<u>6.29</u>	1.42	0.09	0.0037	1.51	<u>0.14</u>	<u>3.90</u>	0.23	0.057	<u>0.28^a</u> (<LOQ)	1.12	<u>0.49</u>	<u>0.071^a</u> (<LOQ)	<u>4.10</u>	<u>1.09</u>	6.42
W2	0.09	1.65	<LOD	0.09	0.0039	0.4	0.041	2.32	<u>1.56</u>	<u>0.0082^a</u> (<LOQ)	<LOD	1.06	0.056	<LOD	0.57	0.019	<u>15.9</u>
W3	0.09	<u>2.08</u>	<LOD	0.23	0.0074	3.26	0.049	2.28	0.45	<u>0.013^a</u> (<LOQ)	<LOD	1.09	0.018	<LOD	<u>1.76</u>	0.0091	<u>45.1</u>
W4	0.09	<u>5.76</u>	<u>0.04^a</u> (<LOQ)	0.14	<LOD	0.43	0.04	<u>6.52</u>	0.39	0.052	<LOD	1.10	0.023	0.16	1.08	<u>0.14</u>	<u>4.64</u>
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	<u>2.77</u>	<LOD	0.27	0.012	2.81	0.0601	2.54	<u>1.80</u>	0.023	<LOD	1.07	0.03	<LOD	<u>1.31</u>	<u>0.036</u>	<u>30.4</u>
E3	0.09	<u>1.83</u>	0.06	0.11	0.0060	0.99	0.084	2.73	<u>3.05</u>	0.023	<LOD	1.06	0.033	<LOD	<u>1.38</u>	0.063	11.6
E4	0.09	1.75	0.07	0.09	<u>0.0015^a</u> (<LOQ)	0.28	0.045	2.58	<u>1.69</u>	0.028	<LOD	1.05	0.017	0.074	<u>1.29</u>	0.092	5.09
E5	0.1	1.70	<u>0.05^a</u> (<LOQ)	0.76	0.0034	0.44	0.053	1.84	<u>1.58</u>	0.0301	<LOD	1.15	0.026	<LOD	0.99	0.057	8.93
BLANK	0.09	1.68	<LOD	0.49	0.0096	<u>8.17</u>	0.0602	2.29	0.72	<u>0.013^a</u> (<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%.

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

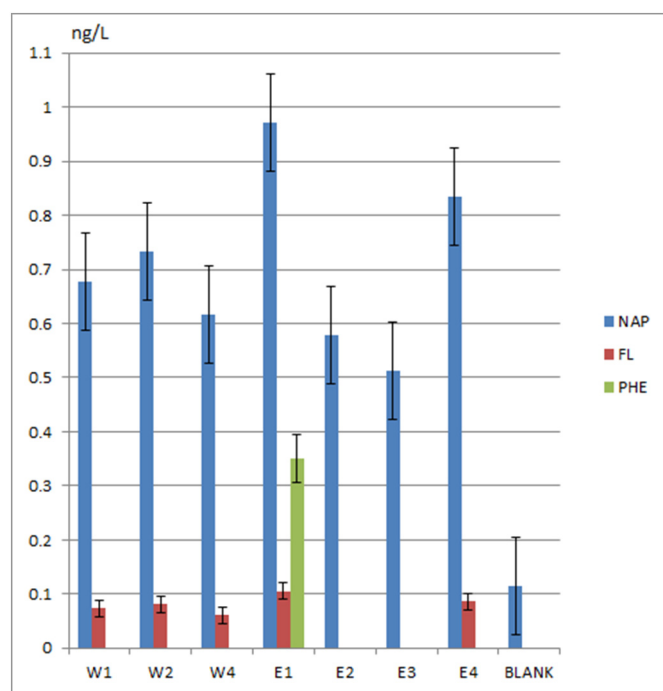


Fig. 3. PAH concentration values in individual snow samples (ng/L). Abbreviations: NAP-naphthalene; FL-fluorene; PHE-phenanthrene.

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.

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).

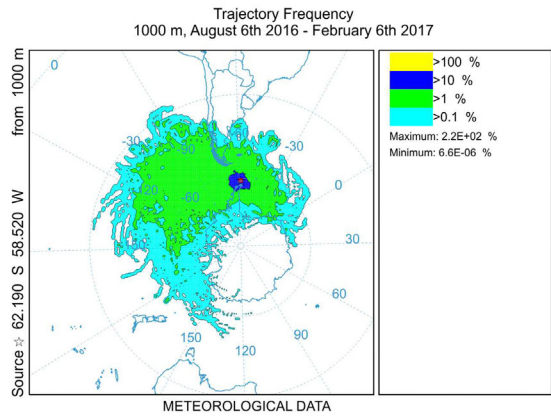
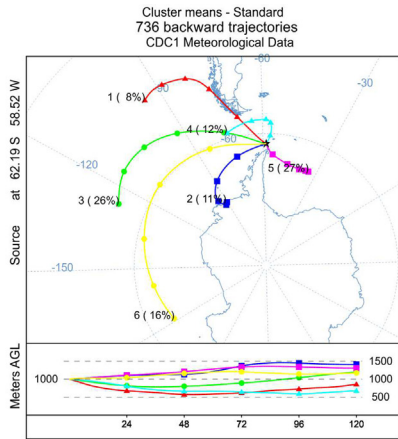
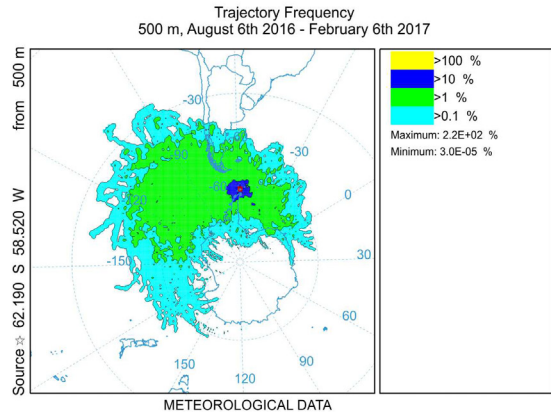
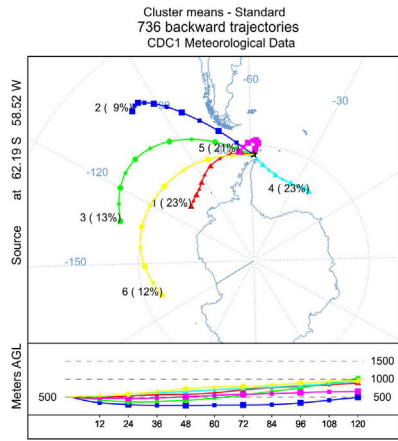
5. Discussion

5.1. Inorganic chemicals in snow cover and its sources

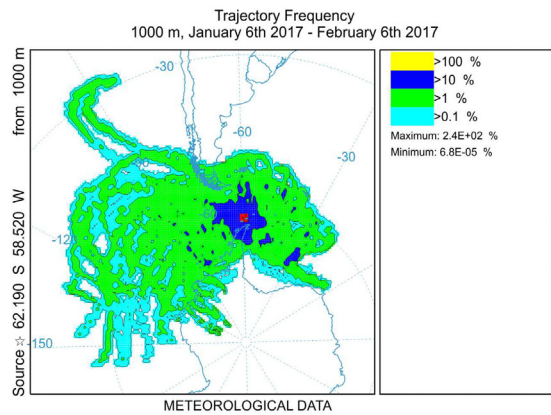
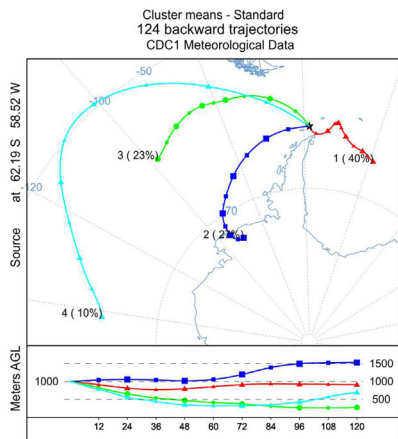
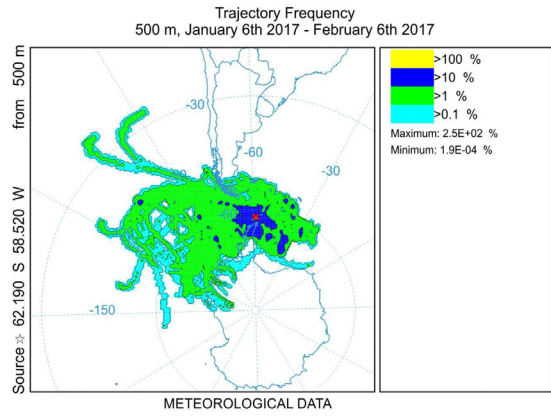
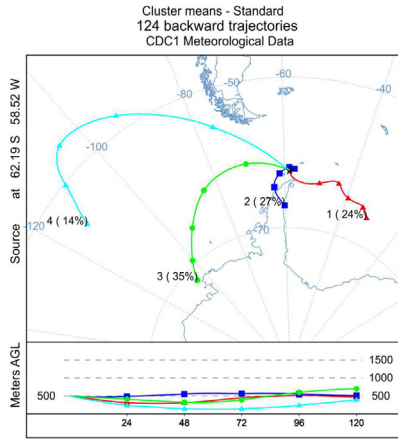
Szopińska et al. (2018), (2019), and Potapowicz et al. (submitted, Part 1) reported results of chemical analysis in the forefield of the Warszawa Icefield at the western shore of Admiralty Bay. This study aims at identifying possible sources of chemicals obtained in the ice-free areas. Previous results 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 nsSO_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 nsSO_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

A



B



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; Szumińska 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 $\mu\text{g/L}$, 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 $\mu\text{g/L}$, 0.57–4.10 $\mu\text{g/L}$, 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 $\mu\text{g/L}$ (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, FI, 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		NAP, PHE, FI, ACP, FLU		
David Glacier, Vitoria Land, EA	14 ng/L		NAP, PHE, FI, ACP, FLU		
Mid Point, Vitoria Land, EA	140 ng/L		NAP, FI, ACP, PHE, FLU		
GV5 Itase, Vitoria Land, EA	1.2 ng/L		PHE, FI, BaP, FLU		
Western shore of Admiralty Bay (KGI), glacier forefield	6.78 ng/L	Surface snow	FI, 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 – acenaphthene, 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 (Pudęłko et al., 2018; Sziło 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

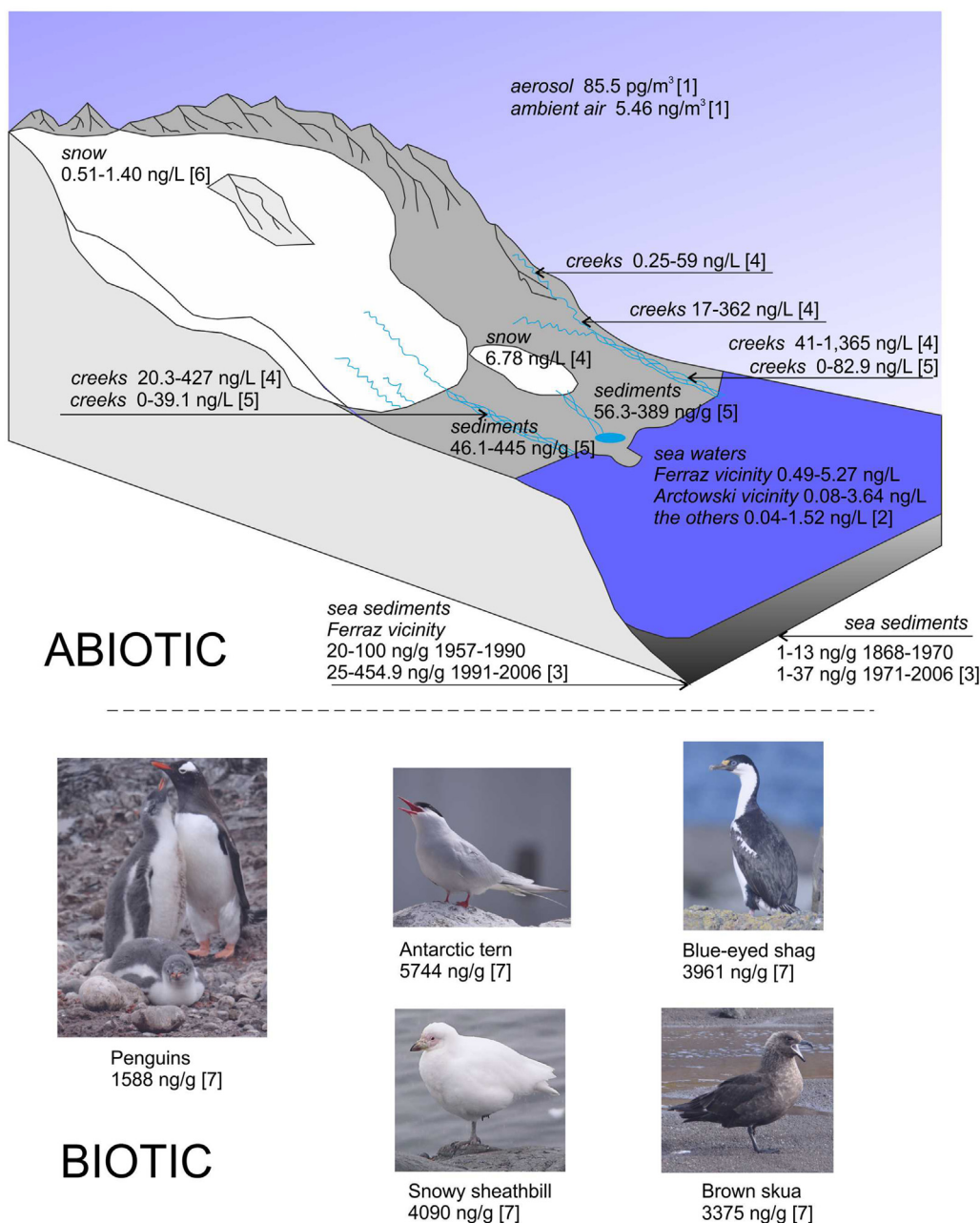


Fig. 5. ΣPAHs concentrations in abiotic and biotic environments at Admiralty Bay (King George Island): aerosol pg/m³, air – ng/m³, water and snow samples – ng/L, sediment samples – ng/g, Antarctic seabirds' fat tissues – ng/g lipid weight (sources of data: [1] Cabrerizo et al. (2014) – Supporting information; [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 (Mão 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 Weight 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 Maritima 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

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.149054>.

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