Impact of a newly-formed periglacial environment and other factors on fresh water chemistry at the western shore of Admiralty Bay in the summer of 2016 (King George Island, Maritime Antarctica)

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HIGHLIGHTS

- Water chemistry in zones recently and historically uncovered by glaciers differs
- PCA analysis covers aerosol influence and chemical weathering.
- Ornithologists and Moss Creek waters influenced by biological factors (higher PO43−, NO3−, NH4+)
- Anthropogenic influence needs monitoring, esp. in terms of heavy metals occurrence.

GRAPHICAL ABSTRACT
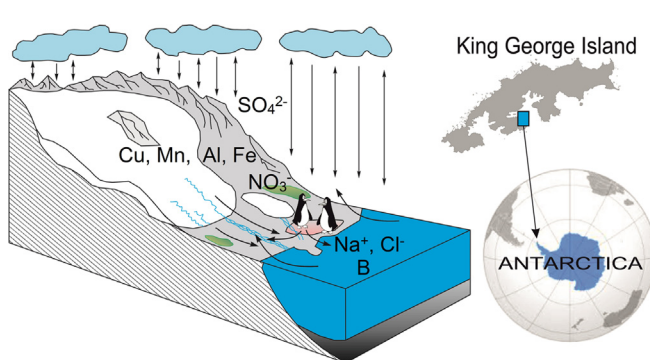
abstract

This study provides a comprehensive analysis of the inorganic chemistry of flowing water at the western shore of Admiralty Bay. In the water samples, ions, and major and trace metals (and B) were detected and quantified. Ad-ditionally, the parameters of pH, specific electrolytic conductivity (SEC_{25}) and total organic carbon (TOC) were determined. Moreover, multivariate data set was created and Principal Component Analysis (PCA) was per-formed. Generally, the water has low total content of the measured mineral constituents b 100 mg L^{-1}. PCA anal-ysis we distinguished two groups of chemical variables shaping water chemistry in the investigated creeks: I –components of marine aerosol origin (presence of Na^+, Cl^- and B) and II – those associated with chemical weathering processes (presence of Al and Fe). Furthermore, the results showed that the flowing water in the newly-formed periglacial areas (formed over the last 30 years) are rich in easily soluble Al and Fe and have lower total measured contents of mineral constituents during the summer period than creeks in non-glacial catchments. Permafrost influence on water chemistry is difficult to identify. The rather insignificant difference between TOC concentrations in waters during summer indicates that permafrost is not a store of organic matter in the studied area. Moreover, local biological factors (lichens and mosses) and those limited to the sea-shore

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vicinity (seabirds and mammals activity) are significant sources of PO_4^{3-}, NO_3^-, and NH_4^+. Despite the described geological and biological features influencing water chemistry, the impact of anthropogenic activity still needs to be verified, especially in terms of heavy metal concentrations.

1. Introduction

Various effects of climate changes (e.g. retreat of glaciers, permafrost degradation) have been observed in recent decades in the Antarctic Peninsula (Guglielmin and Vieira, 2014; Kejna, 1999; Kejna et al., 2013a). This area has been subject to one of the most rapid warming phases on Earth in the last few decades (Vaughan et al., 2003; Turner et al., 2005; Vieira et al., 2008; Mulvaney et al., 2012; Bockheim et al., 2013) and provides a unique opportunity to better understand the impact of global climate on glaciers and permafrost, as well as on related ecosystems (Guglielmin, 2011; Bargagli, 2008).

In the research area, hydrological changes directly related to deglaciation strongly influence the conditions of life, while bedload transport alters the geomorphology of the place. Since its establishment in 1979, the area has undergone a number of changes, in which the process of deglaciation has played an important role. For instance, Simões et al. (1999) suggested that King George Island has lost about 7% of its original ice cover. The distribution of glaciers on the western shore of Admiralty Bay makes this region very interesting (Fig. 1). The glaciers located at the Warsaw Icefield are diverse in terms of the glacial deposits they supply and the intensities of their sediment transport. The following glaciers are located in the area of interest: Ecology, flowing into Suszczewski Bay; Sphinx, whose forehead has rested on flat land since 1977; and the Tower and Windy glaciers on the border of the study site, and from which fresh water flows down a steep slope into the Bransfield Strait. Finally, there is also the Baranowski glacier, until recently a tidewater glacier, whose recession uncovered almost 0.73 km² of surface area, establishing many new riverbeds in the process (see Siłło and Bialik, 2017). The observed retreat of glaciers (Birkenmajer, 2002; Cook et al., 2005; Rückamp et al., 2011; Sobota et al., 2015; Oliva and Ruiz-Fernández, 2016; Pętlicki et al., 2017; Siłło and Bialik, 2017) gives rise to new ice-free areas with intense inflow of glacier meltwater and considerably dynamic geomorphological processes (Oliva and Ruiz-Fernández, 2015, 2016) which is associated with, among others, the formation of drainage networks (Mink et al., 2014; Fountain et al., 2014). The processes in question affect not only the hydrological status of water, but may also constitute a cause for changes in water chemistry. Thus, changes in the chemical composition of water may be seen as a direct indicator of transformations occurring within the cryosphere (e.g. glaciers and permafrost). On the recently deglaciated terrain, weathering processes may be observed. Anderson et al. (2000) pointed out that studies of chemical denudation of glaciated basins indicate that solute fluxes in those areas are above the global mean rate. Chemical weathering in glacial environments causes an increase in bioavailable nutrients in water, e.g. P and Fe, that can be readily used by organisms in downstream environments (Tranter and Wadham, 2014), which may in turn cause changes in biodiversity in freshwater and marine ecosystems.

The factors changing the water chemistry characteristics are complex. Moreover, the source of the chemical composition within the streams is unclear. Unfortunately, water chemistry remains the least studied element of the ice-free area in the Antarctic Peninsula region (i.e. King George Island, KGI). Studies on the chemical composition of fresh water are limited to only a few publications focused primarily on James Ross Island (Hawes and Brazier, 1991), Livingston Island (Toro et al., 2007) and the western shore of Admiralty Bay (inter alia Wojtuń and Fabiszewski, 1999; Juchnowicz-Bierbasz, 1999; Nędzarek and Pociecha, 2010; Nędzarek et al., 2014, 2015; Zwoliński et al., 2016). Typical analyses of the results tend to be limited to selected parts of water chemistry description (ion, metal concentration, organic composition) and are discussed separately. The available studies concerning freshwater in Antarctica do not seek to interpret the results of comprehensive analyses of water chemistry performed using, for instance, chemometric tools for multivariate data processing.

The main objective of this paper is to identify the factors which shape the water chemistry of the creeks located in the western shore of Admiralty Bay and to determine the potential influence of chemical components on ice-free areas and, consequently, on near-shore marine ecosystems also. Hence, this paper aims to provide an interpretation of the multivariate data base of freshwater samples (ions, metal, TOC, pH, specific electrolytic conductivity). Data evaluation involves both the separate interpretation of specific groups of compounds and the use of state-of-the-art tools for multivariate data analysis (e.g. Principal Component Analysis, PCA). Using such a comprehensive approach allowed water composition to be analysed not only in relation to the location of sampling sites, but also with regard to the impact of various factors altering water composition. The studied environment is one of the most sensitive in the world, which is why description of each factor is important, especially description of naturally occurring factors (periglacial environment) vs. anthropogenic factors. This analysis may help to distinguish the sources of each chemical component between soil background (geochemical factor), marine aerosols, glacier retreat, meteorological conditions and transport of nutrients by biovectors e.g. penguins, and the anthropogenic factor.

2. Materials and methods

2.1. Study area

The study area is located on the western shore of Admiralty Bay (King George Island, South Shetland Islands, Antarctic Peninsula, Fig. 1), which belongs to Antarctic Specially Protected Area 128 (ASPA No. 128). ASPA No. 128 was established in order to protect areas featuring important or unusual assemblages of species, including major colonies of breeding native birds or mammals, against unforeseen and potentially hazardous human activity. King George Island, the largest of the South Shetland Islands, has a surface area of approximately 1310 km², 90% of which is permanently glaciated (Birkenmajer, 2002). The ice-free area has conditions favourable to permafrost processes. Discontinuous permafrost occurs on King George Island as ice-cored moraines, rock glaciers and ice- and sand-wedge polygons at an altitudinal range exceeding 15 m a.s.l. (Bockheim et al., 2013). Permafrost thickness ranges from 20 to 100 cm, whereas the active layer depth is from 50 to 180 cm. Recent studies on the South Shetland Islands show that the permafrost and active layer geomorphic system is most common in the ice-free areas of maritime Antarctica (López-Martínez et al., 2012).

Research was conducted on eight streams flowing in one of the largest ice-free areas on the western shore of Admiralty Bay (Figs. 1, 2). The first three watercourses (Petrified Forest Creek 1.62 km in length, Moss Creek – 0.91 km and Ornithologists Creek – 0.90 km, areas I–III) drain the ice-free area to the south-west and south of the Henryk Arctowski Polish Antarctic Station (Fig. 1). The other studied streams drain the immediate forefield of the Sphinx Glacier – area IV (Sphinx 1 Creek – 0.51 km, Sphinx 2 Creek – 0.65 km, Seal Creek – 0.85 km) and the Baranowski Glacier – area V (Siodlo Creek – 0.31 km). The main geographical features of the investigated sites are presented in the Table 1. The most important differences between the studied areas include the presence of permafrost in the catchments of Petrified Forest
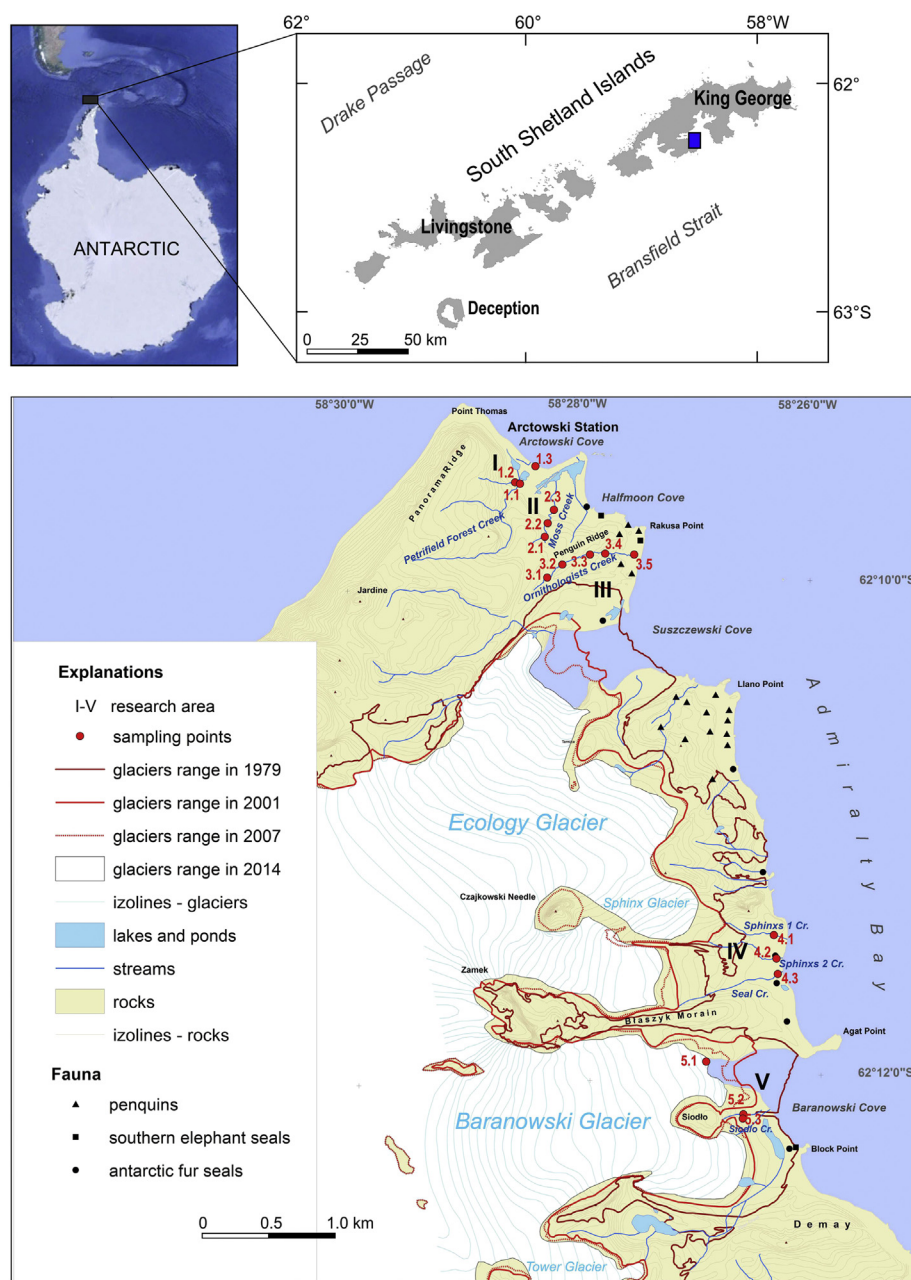
Fig. 1. Map of the western shore of Admiralty Bay (Maritime Antarctica) showing the location of the sampling points and glaciers' retreats between 1979 and 2014. (prepared based on Pudełko, 2008; Landsat image LC82181032014016LGN00 obtained from www.usgs.gov; GoogleEarth application)

Creek, Moss Creek and Ornithologists Creek, and the fact that streams at the forefield of the Sphinx and Baranowski glaciers are fed with glacier meltwaters. No detailed geochemical mapping of the analysed catchments has been carried out to date. Geochemical analyses of individual samples indicate that the volcanic rocks present here are calc-alkaline rocks rich in Al_2O_3, Sr, Rb, and Ba (Birkenmajer et al., 1991). Samples taken in the area of the Baranowski glacier and Jardine Peak (the Petrified Forest Creek catchment) have high Cr contents, while samples from the Baranowski glacier group also have high contents of V, Zr, Zn and Cu (Mozer et al., 2015).

The studied catchments also differ significantly in the occurrence of biogenic factors. Of the analysed streams, Ornithologists Creek stands out markedly for its colony of penguins (and its associated ornithogenic soils). Myrcha et al. (2013) estimated that the penguin population nesting in the Llano Point deposits approximately 5.1 t of phosphorus (P) on land each year. In the Ornithologists Creek valley, the surface

area covered by mosses increases (Fig. 2-area III). The greater share of mosses in the surface area of the outflow section of this stream is related to the impact of the seabird colony, which increases the concentration of nutrients in soils (Zwolicki et al., 2015).

2.2. Meteorological background

Weather and climate conditions on King George Island are characterised by their considerable year—to—year variability, resulting from the interactions between the ocean, sea ice and atmosphere (Kejna et al., 2013a). Based on climate data from the Bellingshausen station for the years 1969–2016 (www.rp5.ru), the mean annual temperature in 2016 was −1.8 °C (Fig. 3A), which is higher than the mean for the entire period (−2.3 °C). Total annual precipitation in 2016 was 560 mm (Fig. 3B), which was lower than the long-term mean, of 697 mm.
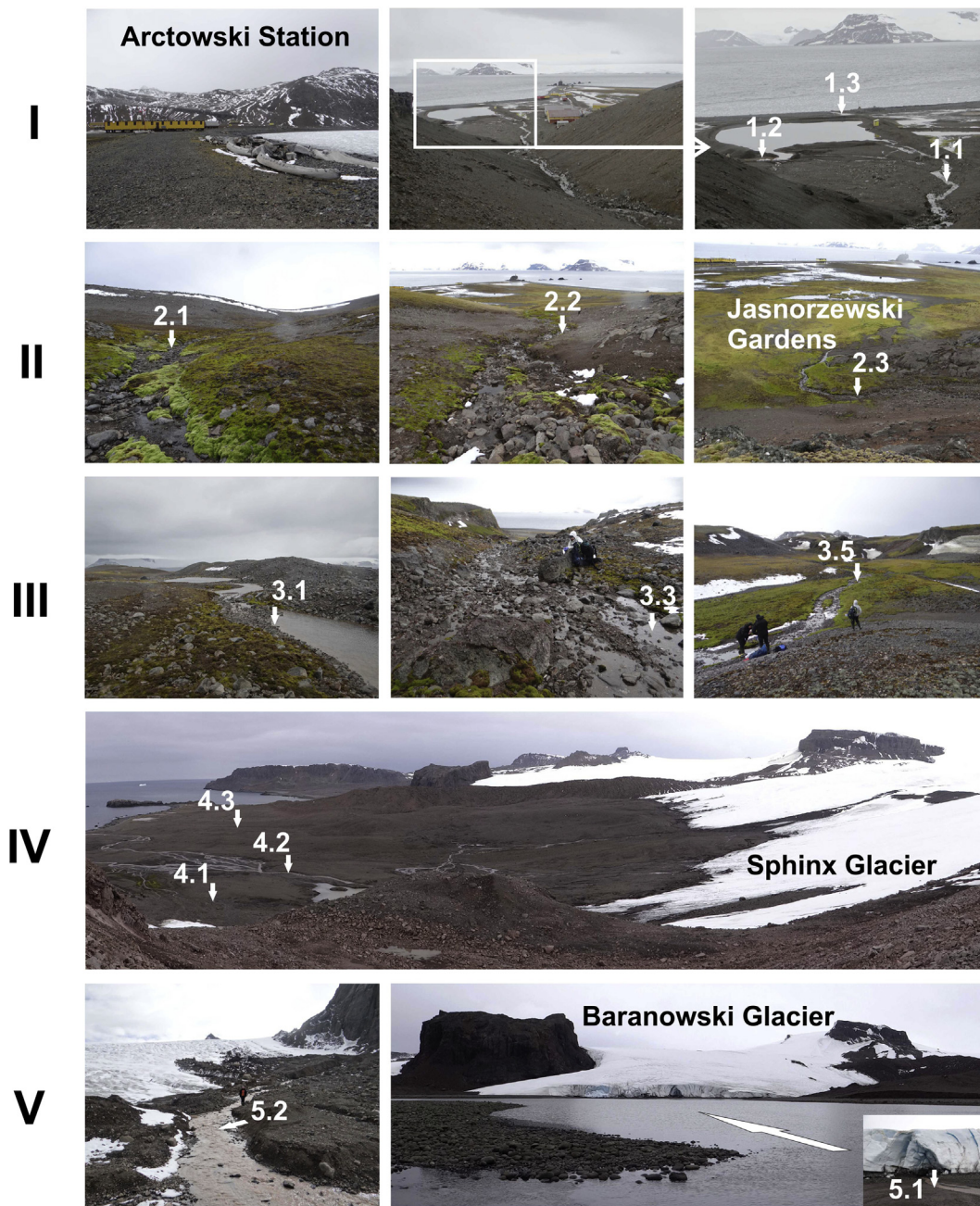
Fig. 2. Sections of the studied creeks at the western shore of Admiralty Bay.

Samples were collected in the austral summer of 2016 (Fig. 3C). At the time preceding sampling, average daily temperatures varied around 0°C in January and 1–2 °C in February (Fig. 3C). The maximum daily temperature (4.7 °C) was noted on March 3rd, and the minimum (−4.1 °C) on February 16th. The snow cover thawed at the end of December 2015 and it rained in the sampling period. Total daily precipitation did not exceed 5–10 mm (Fig. 3C). The most dominant wind directions in the Bellingshausen are northwesterly (30% – NNW, NW, WNW) northerly (10% – N), northeasterly (9% – NE) and southeasterly (8% – SSE) (Fig. 2D). Northerly and westerly directions prevailed in January 2016, whereas in February 2016, in the months preceding sampling, the prevailing winds were northerly, northwesterly and westerly. In the years 2005–2016 and in January and February 2016 the highest speed winds were southeasterly, which do not occur as frequently as northerly and northwesterly ones (Fig. 2D). The wind directions recorded at the H. Arctowski Polish Antarctic Station in 2012 (Kejna et al., 2013b) show the influence of local orographic conditions and the exposure of the western shore of Admiralty Bay towards the south-east. The inflow of pollutants to the study area is limited by the range of circumpolar air circulation, although certain works point out the possibility of long-range air transport of contaminants to the Antarctic, e.g. metallic compounds identified in air at the King Sejong Station (Mishra et al., 2004) and POPs on Dronning Maud Land (Kallenborn et al., 2013), as well as volcanic ashes from Patagonia found in the soil of the Barton Peninsula (Lee et al., 2004).

2.3. Sampling

Water samples were collected from Petrified Forest Creek, Moss Creek and Ornithologists Creek (at three, three and five different points

Table 1
Geographical characteristics of the researched catchments.

No/Name	Description	Hydrology	Geology	Other factors influencing water chemistry
I/Petrified Forest Creek	Petrified Forest Creek 2 (sample 1.1) is a tributary of Petrified Forest Creek. Section 1.2 is in the end of the middle part of the creek, at the border of a quaternary age beach. Section 1.3 is on the beach, down to the pond used as a drinking water reservoir for the Arctowski Station.	Main sources of inflow: snow melt, rain, permafrost thaw Outflow in summer: permanent and ranging from 10 $m^3\ s^{-1}$ to 50 $m^3\ s^{-1}$	Arctowski Cove Formation (basalt lavas, basalt and andesite lavas alternating with fluvial deposits; fossil-bearing terrestrial deposits; laharic agglomerate with basalt lava interlayers); Point Thomas Formation (flow basalts alternating with pyroclastics at the base, followed by lenticular basalt lavas, feldspar phyric tuffs and coarse vent breccias, with subordinate plant-bearing tuffs); Weathering cover transformed by periglacial processes	Permafrost and related processes, e.g. solifluction, cryoturbation (1.1, 1.3); Exposure to impact of tractor and helicopters related to Arctowski station activity (mechanical erosion, possible sources of, e.g., heavy metals)
II/Moss Creek	Sections 1.1 and 1.2 are in the upper and middle course of the creek. Section 2.3 is located in the mouth part, below a step within a small alluvial fan.	Main sources of inflow: snow melt, rain, permafrost thaw Outflow in summer: periodic	Arctowski Cove Formation (as above); Weathering cover transformed by periglacial processes	Permafrost and related processes, e.g. solifluction, cryoturbation; Mosses and *deschampsia* sp.; Skua nests
III/Ornithologists Creek	Sections 3.1 and 3.2 are located along the part of the creek formed below the bifurcation area. Section 3.5 is located in the mouth of the creek, in the bottom part of an alluvial fan.	Main sources of inflow: snow melt, rain, permafrost thaw Outflow in summer: periodic	Arctowski Cove Formation (as above), Point Thomas formation (as above); Moraine deposits, penguin rookeries	Permafrost and related processes e.g. soliflucition, cryoturbation; Penguin rookeries with ornithogenic soils (3.4, 3.5), phosphatised marine terrace (3.5); Skua nests Elephant seals
IV/streams near Sphinx Glacier	Sections 4.1, 4.2 and 4.3 are in the mouth of the three creeks in the forefield of the Sphinx Glacier	Main sources of inflow: glacier melt Outflow in summer: permanent, considerable dynamics of discharges	Zamek Formation (terrestrial basaltic andesite and andesite lava, tuff and andesite agglomerate, with rich fossil plant remains); Llano Point Formation (grey, green and black basaltic andesite lavas, alternating with red scoria, pyroclastic and flow breccias); Moraine deposits (with considerable hydration and low compaction)	Watersheds recently uncovered by glacier; Drainage system in initial phase of development;
V/streams near Baranowski Glacier	Section 5.2 is in a small creek in the forefield of the Baranowski Glacier	Main sources of inflow: glacier melting Outflow in summer: permanent, considerable dynamics of discharges	Llano Point Formation (as above) Moraine deposits (with considerable hydration and low compaction)	Watersheds recently uncovered by glacier; Drainage system in initial phase of development
Literature	–	(Zwoliński, 2007; own observation)	(Birkenmajer, 2003; Schaefer et al., 2007)	(Schaefer et al., 2007; Zwoliński, 2007; Myrcha et al., 2013; Simas et al., 2015)

in each creek, respectively) (Fig. 1). Samples were also gathered at the mouths of the following creeks: Petrified Forest, Sphinx 1, Sphinx 2, Seal and Siodlo.

Sample design was created in such a way as to verify the different factors shaping water chemistry during the austral summer. Samples collected in the vicinity of H. Arctowski Station may provide information inter alia about anthropogenic influence on water bodies (areas I–III). In turn, samples collected at the mouths of the following creeks in the areas IV–V would help to describe changes in the glacier runoff chemistry potentially affecting marine near shore ecosystems. Moreover, samples were collected from selected creeks near the station to check the spatial distribution of chemical compounds (areas I–III). Creeks in areas IV and V have no permanent outflow in the upper and middle course during the summer season, and so we decided to sample the mouth sections of these creeks.

Water samples were collected twice from the selected points in late January and March 2016. The detailed period of sampling is shown in Fig. 3C. Samples were collected manually in a volume of 1 L each. To minimise the risk of sample-contamination (e.g. trace amounts of analytes transferred by humans) samples were collected using polyethylene gloves and were rinsed with stream water three times before filling. Bottles were filled completely without air bubbles to prevent the

loss of analytes to headspace. After sampling, pH and conductivity measurements were performed, and later samples were kept frozen until they were analysed in Poland.

2.4. Laboratory methods

Total organic carbon (TOC) concentration in the studied samples was measured by a TOC-VCSH/CSN Analyser (SHIMADZU, Japan) using the catalytic combustion method with non-dispersive infrared detection (NDIR).

The concentrations of metals and non-metals in water samples were determined by Thermo XSERIES 2 ICP-MS inductively coupled plasma mass spectrometry featuring 3rd generation collision cell technology with discrimination (Thermo Fischer Scientific, Germany). The analysis involved a wide range of elements (Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, Cs, Ba, La, Tl, Pb, Th, U). ICP-MS adjustments were as follows: coll 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} with kinetic energy discrimination (KED).

Ion concentration was obtained by DIONEX 3000 chromatograph (DIONEX, USA). Moreover, we analysed major ions (Na^+, K^+, Ca^{2+},
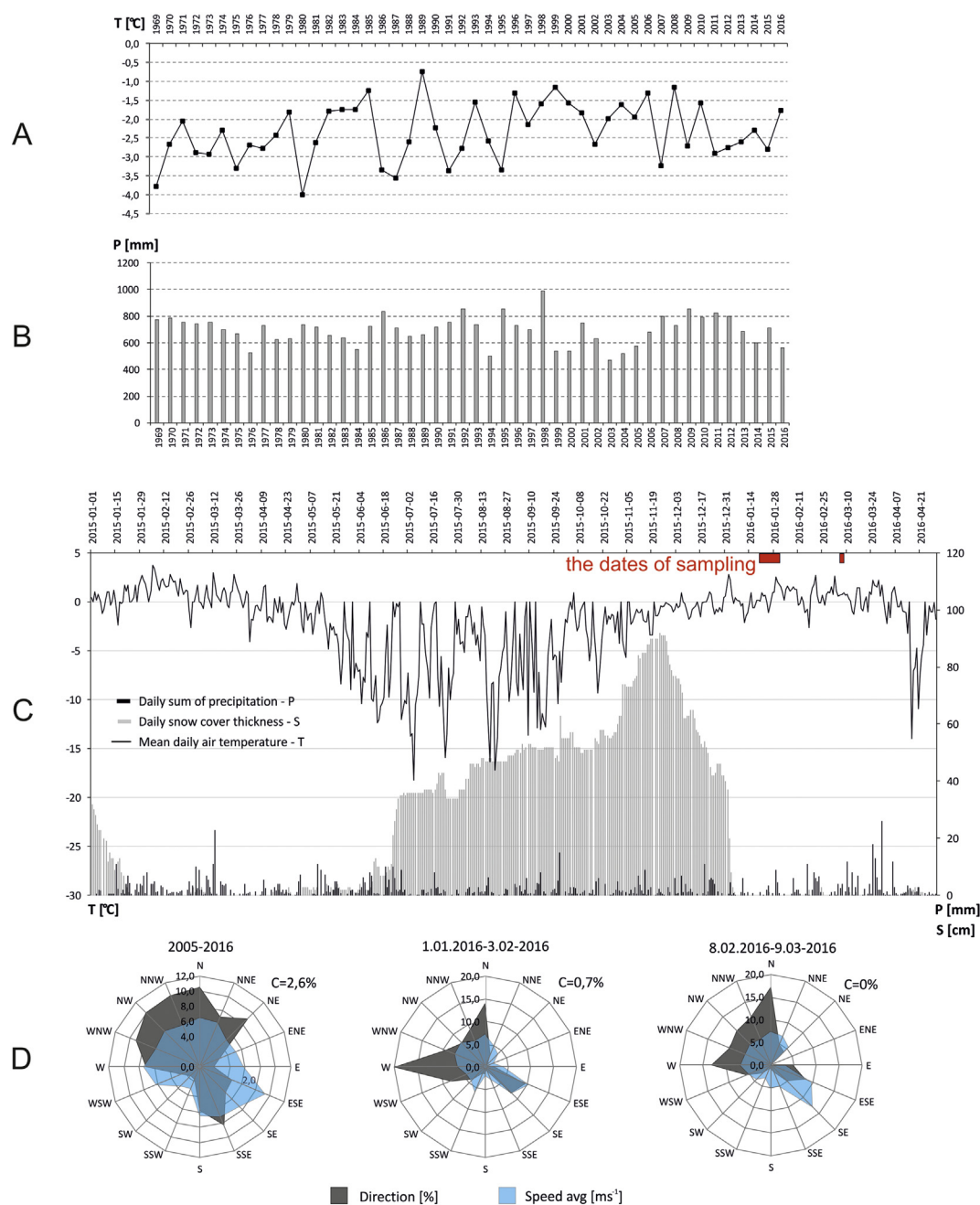
Fig. 3. Climate conditions on King George Island: (A, B) long-term climate record; (C) weather conditions in the period from January 1st, 2015 to April 30th, 2016, and (D) wind directions and wind speed in the period of 2005–2016 and during the months preceding the sampling.
(based on data available on www.rp5.ru, at the Bellingshausen station)

Mg^{2+}, Cl^-, SO_4^{2-}, F^-, Br^-), as well as nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+) and reactive phosphorus (PO_4^{3-}). As far as anion analysis is concerned, a Dionex IonPac AS22 analytical column was used (eluents: 4.5 mM Na_2CO_3 and 1.5 mM $NaHCO_3$, flow rate: 0.3 mL min^{-1}). For cation analysis, meanwhile, we employed a Dionex IonPac CS16 analytical column (eluent: 38 mM methanesulfonic acid, flow rate: 0.36 mL min^{-1}). Conductometric detection for both cation and anion analysis was applied.

Moreover, the contribution of 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).

Specific electrolytic conductivity (SEC_{25}), pH and temperature were measured with a Cx401 (Elmetron, Poland) multi-functional measuring device immediately after sampling.

2.5. Quality assurance/quality control (QA/QC)

All analyses were repeated three times. Standard deviations of triplicate measurements are listed in Appendix A (Tables A.1, A.2 and A.3). Certified standard solutions (Sigma-Aldrich; Inorganic Ventures) were used to assess the accuracy of analytical methods and standard solutions. The limit of detection was in the ranges 0.003–0.3 µg L^{-1}, 0.01–0.09 mg L^{-1} and 0.013 mg L^{-1} for metals (and B), ions and TOC concentration, respectively. The resolution of the Elmetron Cx401

multi-functional device was ± 0.002 for pH; ± 0.1 mV for conductivity and $\pm 0.1\ °C$ for temperature. More information regarding instruments and method description is available in Appendix B.

2.6. Statistical analysis

To detect pair-wise relationships among the metals (and B) and TOC concentration in the investigated water samples, Pearson's correlation coefficients (r) were calculated using Excel 2010 (Microsoft Office, version 2010, U.S.A.). Statistical significance of correlation coefficients was assessed at a significance level of $p < 0.05$. The statistical significance of correlations was verified using the t-Student test. A multivariate dataset was created, and Principal Component Analysis (PCA) was employed to reveal hidden dependences in the data using by MATLAB Version: R2013a with Statistics Toolbox Version 9.1 manufactured by MathWorks, U.S.A.

3. Results

3.1. Basic inorganic analysis

The pH, conductivity values and ion concentrations of the studied water can be found in Table 2, which also contains other results for the western shore of Admiralty Bay available in the literature. The pH in surface water ranged from 5.96 to 8.17 in January and from 5.76 to 7.65 in March, while the highest recorded pH is for the single surface snow sample (9.65). The analysed samples show low total content of the measured mineral constituents (<100 mg L^{-1}). Mineralisation in surface water samples ranged from 4.81 mg L^{-1} to 77.3 mg L^{-1}, while for samples collected at the outflow from the glacier it was in the range of 2.07 mg L^{-1} to 3.51 mg L^{-1}, and in the snow sample 4.24 mg L^{-1} (Table 2). Cl$^-$, Na$^+$ and SO$_4^{2-}$ were found to dominate in the chemical composition of analysed water in both the first and second measurement series. Cl$^-$ ions constituted from 29.3% to 45.3% of total sum of ions expressed as meqL^{-1}, Na$^+$ ions from 27.1% to 45.8%, and SO$_4^{2-}$ ions from 5.5% to 16.5%. The combined sums of these three ions constituted from 73.1% to 97.1% of the sum of all ions in meqL^{-1} (Appendix A, Table A.2, ions concentration given in mgL^{-1}).

Percentage of nss SO$_4^{2-}$ in the studied samples varied from 20.3% to 67.49% and from 24.70 to 70.27% for January and March, respectively (Appendix A, Table A.4). In most studied sites the percentage of nss SO$_4^{2-}$ did not differ between January and March (difference $<13\%$) excluding sites no. 2.1 and 4.3, where the difference is $>25\%$.

Moreover, special attention needs to be paid to concentrations of NO$_3^-$ in Ornithologists Creek, which ranged from 0.653 to 6.15 mg L^{-1} and from 0.408 to 13.6 mg L^{-1} in January and March, respectively (Table 2). One should also note the increased (compared to other data) concentration of various forms of nitrogen (NO$_2^-$ and NH$_4^+$) observed in Ornithologists Creek (section below point 3.4). The concentrations of NO$_2^-$ for this point were 3.80 mg L^{-1} and 8.81 mg L^{-1} in January and March, respectively. The concentrations of NH$_4^+$ in Ornithologists Creek were found to be in the range of 0.021–0.232 mg L^{-1} and 0.062–0.092 mg L^{-1} in January and March, respectively. However, at the majority of points in March the concentrations were under the limit of detection. Concentrations of PO$_4^{3-}$, on the other hand, fall within the range of 0.403–0.411 mg L^{-1} and 0.325–1.28 mg L^{-1} for Moss Creek and Ornithologists Creek, respectively.

3.2. Trace metal and total organic carbon analysis

The presented results (Fig. 4) indicate that in the majority of studied samples total base metal concentration can be classified as low and as such is independent of pH. However, samples taken from Ornithologists Creek (3.5) in January and March, as well as samples collected in January from the creek at the forefield of the Baranowski Glacier (5.2) have higher contents of base metals in the pH range of 6.25 to 7.62

than the remaining samples. All three samples were gathered at the creeks' mouth sections.

The ranges of organic matter concentration (measured as TOC) are 0.013–0.199 mg L^{-1} and 0.015–0.373 mg L^{-1} in January and March, respectively. The highest concentrations are observed in Ornithologists Creek (3.4) in January and in the water reservoir (1.3) in March. The lowest concentrations are observed in the creeks near the Baranowski Glacier (5.2, January) and (5.1, March) (Appendix A, Table A.2). Moreover, TOC values were compared with concentration of metals and B (Table 3). Table 2 presents the results of the entire data set (obtained in March and January 2016). Appendix C.1 and C.2 indicate correlations between TOC and metals and non-metal for separately analysed March and January data sets. Strong correlations ($0.6 < |r| < 0.8$) between TOC and B (0.698), TOC and Rb (0.696) (Table 2) were found. Moreover, we can indentify significant strong and very strong positive correlations between TOC and Rb, and between TOC and B, Ni, Rb, Ag, La, Pb, Th for January and March data sets, respectively (Appendix C.1 and C.2).

Looking at the levels of particular metal contents (Appendix A Table A.1) higher concentrations of P, Sr, Cu and Zn have been observed in the samples taken from Ornithologists Creek (especially sample 3.5, from the mouth section). In section 3.5, the ranges of concentrations of P, Sr, Cu and Zn during the austral summer are: 113–214 μg L^{-1}; 8.61–21.0 μg L^{-1}; 3.65–5.81 μg L^{-1}; 7.58–19.7 μg L^{-1}, respectively. Furthermore, very strong correlations ($0.8 < |r| \leq 1$) have been observed in the following pairs of metals: Al and Fe (0.982), Co and Mn (0,864), Zn and Cu (0.887) (Table 2). In January very strong correlations were indicated between the following pairs of metals: Li and V, U; Al and Fe; V and U; Zn and Cu, Th; Co and Tl, Th; Cu and Th; Ba and Ga (Appendix C.1). In March very strong correlations were observed in the following pairs of metals and non-metals: Li and Sr, Cs; B and Rb, Th; Al and V, Tl; Mn and Co, Zn, Cd; Fe and Tl; Co and Cd; Ni and Ag, Pb; Cu and Rb, Pb; Zn and Cd; Ga and U; Pb and Ag, Sr; (Appendix C.2).

3.3. Multivariate data analysis result

PCA was performed separately for data series from both January and March. In addition, the third case, in which the two series were combined, was examined in order to demonstrate possible changes in the water's chemical composition. All 39 hydrogeochemical variables have been taken into account in the analysis. The considered variables include major ions, metals (and B), pH, water temperature (T) and TOC. In the January data, two principal components were identified that represent $>90\%$ of the variance (Fig. 5A). PC1 was found to have a strong positive correlation with Al and Fe, and PC2 with Na$^+$, Cl$^-$ and B. In the March data, three principal components were obtained in which PCs 1 and 2 represent $>72\%$ of the variance (Fig. 5B). In contrast to the first series PC1 was strongly positively correlated with Na$^+$, Cl$^-$ and B (and had no strong negative correlations), while PC2 was strongly correlated with Mn, Sr and NO$_3^-$ and correlated negatively with Al and Fe. For the entire data set, PC1 and PC2 represent 81% of the variance (Fig. 5C). PC1 is strongly positively correlated with Fe and Al and strongly negatively correlated with Na$^+$, Cl$^-$ and B. Plot C clearly shows the significant influence of these two groups of chemical variables on the studied water chemistry characteristics.

4. Discussion

4.1. Influences of newly-formed periglacial environment on water chemistry (glacier retreat, permafrost, and geology)

Regional climate conditions on King George Island (Maritime Antarctic) have led to intense glacier retreat and permafrost degradation. This has resulted in increased geomorphic dynamics and sediment transfer from slopes and plateaus to the seacoast (Bockheim et al., 2013). Owing to the considerable rate of glacier retreat in the second half of the 20th century, the area in question was uncovered only

Table 2
Major chemical properties of fresh water collected at the western shore of Admiralty Bay.

Sampling place	Sampling period	SEC_{25} [µS cm^{-1}]	pH [−]	Na$^+$ [mg L^{-1}]	NH$_4^+$	K$^+$	Ca^{2+}	Mg^{2+}	F$^-$	Cl$^-$	Br$^-$	NO$_3^-$	NO$_2^-$	PO$_4^{3-}$	SO$_4^{2-}$	References
Ornithologists Creek	Apr 1990–Dec 1993	166.48	n.d.	19.55	n.d.	1.95	4.6	2.67	n.d.	30.4	n.d.	n.d.	n.d.	n.d.	13.0	Zwoliński et al., 2016
Ecology Creek	Apr 1990–Dec 1993	107.15	n.d.	15.64	n.d.	0.39	3.6	1.22	n.d.	25.1	n.d.	n.d.	n.d.	n.d.	6.24	
Petrified Forest Creek	Jan–March 2005															Nędzarek et al., 2015
Upper part		172.2	7.89	19.9	0.021	0.278	3.80	2.99	0.016	37.1	n.d.	0.271	0.011	n.d.	6.40	
Mouth		186.9	7.91	22.6	0.014	0.302	4.63	4.04	0.013	42.9	n.d.	0.330	0.006	n.d.	5.87	
Ornithologists Creek																
Upper part		126.9	7.51	16.5	0.034	0.277	2.82	3.15	0.023	29.4	n.d.	0.678	0.025	n.d.	4.87	
Mouth		216.5	6.66	23.5	0.130	1.34	6.44	4.55	0.292	38.0	n.d.	11.2	0.179	n.d.	12.9	
Stream near Ecology Glacier																
Upper part		53.9	7.39	7.38	0.023	0.125	1.90	1.06	0.025	13.1	n.d.	0.229	0.025	n.d.	2.08	
Mouth		90.9	7.57	12.2	0.022	0.156	2.38	1.10	0.016	21.5	n.d.	0.255	0.016	n.d.	3.63	
Drinking water reservoir		165.6	7.81	18.1	0.041	0.262	3.40	2.64	0.023	33.0	n.d.	0.279	0.031	n.d.	5.86	
Petrified Forest Creek	Jan 2016															Our study Sample no.
Mouth		98.5	7.87	16.3	<LOD	0.166	0.078	0.284	0.081	24.1	0.289	0.494	<LOD	0.440	13.8	1.1
Mouth		45.3	8.17	5.41	0.028	0.050	0.057	0.077	<LOD	9.08	0.114	0.200	<LOD	<LOD	3.65	1.2
Outflow, after water reservoir		117.3	7.02	21.9	0.155	0.832	0.788	0.624	<LOD	31.0	0.188	0.013	<LOD	<LOD	9.19	1.3
Moss Creek																
Upper part		11.8	6.14	1.28	0.051	0.076	0.037	0.059	<LOD	2.36	0.048	0.029	<LOD	<LOD	0.880	2.1
Middle		31.7	6.49	3.91	0.061	0.049	0.044	0.045	<LOD	6.06	0.079	0.198	<LOD	0.411	2.28	2.2
Mouth		42.0	6.50	5.61	0.021	0.124	0.047	0.068	<LOD	9.51	0.115	0.250	<LOD	0.403	3.17	2.3
Ornithologists Creek																
Upper part		66.0	6.82	10.2	<LOD	0.173	0.271	0.324	<LOD	13.9	0.075	0.700	<LOD	0.324	3.02	3.1
Middle		78.6	6.86	12.1	0.077	0.274	0.895	0.648	<LOD	15.7	0.108	0.653	<LOD	0.318	3.47	3.2
Middle		71.1	6.76	10.2	<LOD	0.256	0.623	0.461	<LOD	14.7	0.104	0.829	<LOD	0.385	3.17	3.3
Middle		82.7	6.83	9.98	0.232	0.485	0.765	0.543	0.112	19.2	0.103	3.80	<LOD	0.386	6.16	3.4
Mouth		96.3	6.74	13.0	0.130	1.32	1.70	0.986	0.129	17.9	<LOD	6.15	<LOD	0.897	7.68	3.5
Streams near Sphinx Glacier																
Sphinx-1		136.7	7.38	20.0	<LOD	0.098	2.21	0.696	<LOD	26.6	0.171	0.044	<LOD	0.314	5.50	4.1
Sphinx-2		137.0	7.18	22.1	<LOD	0.112	4.58	0.499	<LOD	28.9	0.221	0.073	<LOD	<LOD	5.89	4.2
Seal (mouth)		73.6	7.26	6.16	<LOD	0.060	3.30	0.400	<LOD	11.2	0.05	<LOD	<LOD	<LOD	2.20	4.3
Streams near Baranowski Glacier																
1 (outflow from the glacier)		15.7	5.96	0.982	<LOD	0.040	0.060	0.046	0.073	1.20	0.053	<LOD	<LOD	0.375	0.692	5.1
2 Siodlo		90.7	7.62	5.06	<LOD	<LOD	3.47	0.534	<LOD	10.6	<LOD	<LOD	<LOD	<LOD	3.54	5.2
Surface snow near Baranowski Glacier		155.4	9.65	1.18	<LOD	<LOD	0.064	0.038	<LOD	1.61	<LOD	0.282	<LOD	0.678	0.380	5.3
Petrified Forest Creek	March 2016															
Mouth		133.8	7.31	21.5	<LOD	0.335	1.95	1.30	<LOD	32.3	0.338	0.337	<LOD	0.294	9.01	1.1
Mouth		127.0	7.19	18.3	<LOD	0.205	2.40	1.44	0.080	26.7	0.213	0.288	<LOD	0.344	5.33	1.2
Outflow, after water reservoir		156.7	7.40	27.4	0.258	2.10	1.27	0.726	0.085	34.4	0.312	<LOD	<LOD	0.803	10.0	1.3
Moss Creek																
Upper part		118.4	6.81	17.2	<LOD	0.457	1.83	1.59	0.082	26.4	0.189	1.33	<LOD	0.368	6.02	2.1
Middle		103.2	6.91	14.7	<LOD	0.340	1.64	1.12	0.081	21.8	0.266	0.873	<LOD	0.410	7.01	2.2
Mouth		110.5	7.06	13.4	<LOD	0.525	1.86	1.39	0.090	23.9	0.248	0.966	<LOD	0.399	9.49	2.3
Ornithologists Creek																
Upper part		90.9	7.14	13.3	<LOD	0.263	0.602	0.614	<LOD	17.8	0.145	0.675	<LOD	0.397	3.84	3.1
Middle		98.3	7.13	7.12	0.062	0.317	1.37	1.02	0.081	12.0	0.113	0.408	<LOD	0.352	2.22	3.2
Middle		97.0	7.01	11.8	<LOD	0.202	0.780	0.512	0.105	20.3	0.178	1.81	<LOD	0.438	4.33	3.3
Middle		95.4	6.76	16.9	<LOD	1.08	2.39	1.43	0.215	22.2	0.228	8.81	<LOD	0.516	8.01	3.4
Mouth		80.0	6.28	16.6	0.092	1.60	2.57	1.52	0.269	22.7	0.221	13.6	<LOD	1.28	10.7	3.5
Streams near Sphinx Glacier																
1		78.1	7.44	11.5	<LOD	0.074	1.21	0.363	<LOD	14.2	0.211	<LOD	<LOD	<LOD	2.91	4.1
2		78.4	7.49	12.0	<LOD	0.068	1.30	0.143	0.411	12.7	0.167	0.468	<LOD	0.768	3.20	4.2
3		86.6	7.54	4.36	0.118	0.062	2.29	0.252	<LOD	7.25	0.067	<LOD	<LOD	0.352	2.31	4.3
Streams near Baranowski Glacier																
1 (outflow from the glacier)		5.1	5.76	0.701	<LOD	<LOD	0.040	0.030	<LOD	0.868	<LOD	<LOD	<LOD	0.295	0.146	5.1
2		112.3	7.65	7.40	<LOD	0.044	3.87	0.673	0.090	12.2	0.161	0.141	<LOD	0.529	3.99	5.2

Abbreviations: <LOD – below limit of detection, n.d – not determined, SEC_{25} - specific electrical conductance.

recently (Fig. 1). In consequence, the drainage network is still developing and has considerable dynamics, which also explains the intensity of hydrochemical processes within the moraine material. The material is of small compactness, which favours a marked fluctuation in moisture – from high hydration during ablation, snowmelt and rainfall to increased drying of the surface layer, particularly in the vicinity of micro-uplift slopes. Such a dynamic change in conditions favours enrichment of suspended sediments in relatively insoluble elements, such as Fe and Al (Brown, 2002; Tatur and Keck, 1990). Thus, as Al and Fe are leached, water becomes enriched in these elements as well. Glaciarised drainage basins (IV, V) may be subject to higher rates of mechanical erosion, which greatly exceed rates of chemical weathering (Anderson et al.,
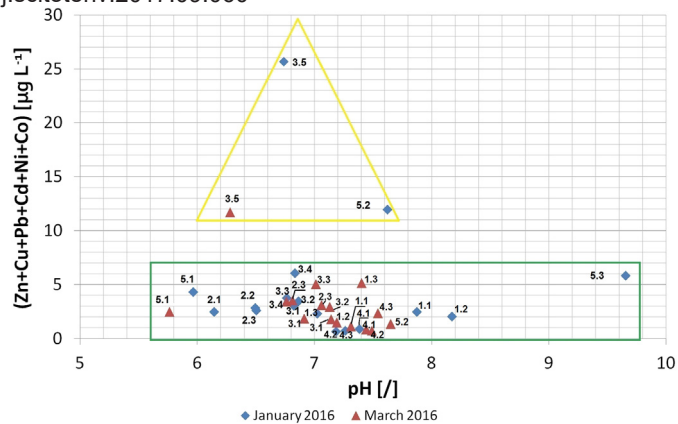
Fig. 4. Ficlin Diagram for studied water samples.

2000) (Fig. 6a, b). Therefore, the difference between chemical weathering of Al and Fe in the flowing water in areas I–III and IV–V may be associated with the composition of suspended material transported in glacial and non-glacial catchment areas (Brown, 2002). Based on our field observation, creeks in areas IV and V transport much more suspended material than creeks in areas I–III. Moreover, the snow cover sample collected in January at the forefield of the Baranowski glacier was found to have the highest pH (9.65), which is not typical of precipitation water, whose pH tends to be neutral or weakly acidic. Such high pH may be related to the processes of rock weathering and subsequent transport of mineral particles onto snow patches by wind (Fig. 6c). The chemical composition of water samples may also have been altered as a result of rock weathering. Due to the fact that the environment of King George Island is rich in pyrite (Paulo and Rubinowski, 1987), the following reaction could occur: (1) $4FeS_2(s) + 14H_2O(l) + 15O_2(aq) \longleftrightarrow 16H^+(aq) + 8SO_4^{2-}(aq) + 4Fe(OH)_3(s)$ (Brown, 2002). However, after Hodson et al. (2010) it is suggest to check carbonate weathering and to couple it to pyrite oxidation, to verify this hypothesis. Nevertheless, the phenomenon described above shows the intensity of weathering in the area of recently uncovered moraine surfaces (areas IV–V), which affects the chemical composition of flowing water.

Water–rock interactions and chemical weathering rates are usually high and often considerably more significant than anthropogenic impact in areas of glacial and periglacial processes (Brown, 2002). Moreover, in the summer time the so-called "spring pulse" can be observed at the beginning of the season, which translates into an increase in concentrations of various components in fresh waters. This is due to the fact that throughout winter the components of precipitation (ions, metals, organic matter) are stored in the snow cover. Thus, (1) during snowmelt they are released with meltwater (Waldner and Burch, 1996; Szopińska et al., 2016a) (2) when the "spring pulse" occurs there is first a high energy stream flow that erodes particles and solutes in the catchment; hence, observation of this phenomenon is especially important in terms of the release of nutrients into the environment. That is why samples were collected both at the beginning of the "spring pulse"—in January—and at the end of austral summer, in March. The "spring pulse" phenomenon can be observed in the variation in organic matter concentration measured as total organic carbon concentration. A higher concentration of TOC in flowing water was recorded in January in Ornithologists Creek (Appendix A, Table A.3), in whose lower course ornithogenic soils occur (Nędzarek et al., 2014). In this area we can observe the occurrence referred to as "spring pulse", which is evident in the higher concentration of TOC in the lower course of the stream (point 3.4 and 3.5). This is mostly related to intense snow-cover melting (Fig. 3C). Moreover, TOC concentration in March in the watercourse at the forefield of the Baranowski glacier was double that of the samples collected in January. This is likely a result of increased melting of the

Baranowski glacier (Sziło and Bialik, 2017) and sediment release, rather than of processes related to the release of organic matter from permafrost degradation. The lack of a significant difference in terms of TOC concentration in January and March (varying in the ranges 0.16–018 mg L^{-1} and 0.17–0.20 mg L^{-1}, respectively, Appendix A: Table A.3) in watercourses at the forefield of the Sphinx glacier may arise from the fact that the samples were taken one day before (January 19th) the sampling at the forefield of the Baranowski glacier (January 20th), and there had been no precipitation for several days prior to that (Fig. 3C). However, in comparison to other results found in the literature (e.g., Nędzarek and Pociecha, 2010), where TOC was measured in the freshwater systems of the Thomas Point Oasis (TOC range: 91.38–26.90 mg L^{-1}), the obtained concentrations of TOC (1.38–26.90 mg L^{-1}, Appendix A, Table A.3) can be classified as low.

Concentration of metals in water samples depends also on the presence of organic matter. Organic matter can change the hydrogeochemical cycles of trace elements via mechanisms of chemisorption, as well as via complexation and/or chelation on organic matter and mineral particles (Nędzarek et al., 2014; Szopińska et al., 2016b). Strong correlations ($0.6 < |r| < 0.8$) between TOC and B (0.698), TOC and Rb (0.696) (Table 3) were found across all study areas. Both B and Rb constitute elements that can be leached from, inter alia, volcanic rocks (e.g., Kot, 2015; Faure, 2001). Moreover, we found significant positive strong and very strong correlations between TOC and Rb; and between TOC and B, Ni, Rb, Ag, La, Pb, Th for January and March data sets, respectively (Appendix C.1 and C.2). However, although Ni and Pb are both heavy metals, positive correlation between TOC and Ni, and between TOC and Pb appears to have only a minor impact on the shaping of water chemistry, owing to the fact that concentrations of TOC, and of Ni and Pb, were found to be low, bordering on the detection limit (Appendix A, Table A.1). Moreover, La, Ag and Th were also determined to be close to detection limits, and hence their contribution to the geochemical properties of studied water samples is negligible (Appendix A, Table A.1). The strong correlation between TOC and Rb in January and March clearly indicates that this phenomenon confirms the natural origin of Rb in water, especially from the calc-alkaline rocks that are rich in Al$_2$O$_3$, Sr, Rb and Ba (Birkenmajer et al., 1991). The stronger correlation between TOC and B in March may indicate a general marine influence on water chemistry rather than releasement of boron together with the organic matter. The presence of boron in water samples is more fully described in paragraph 4.3.
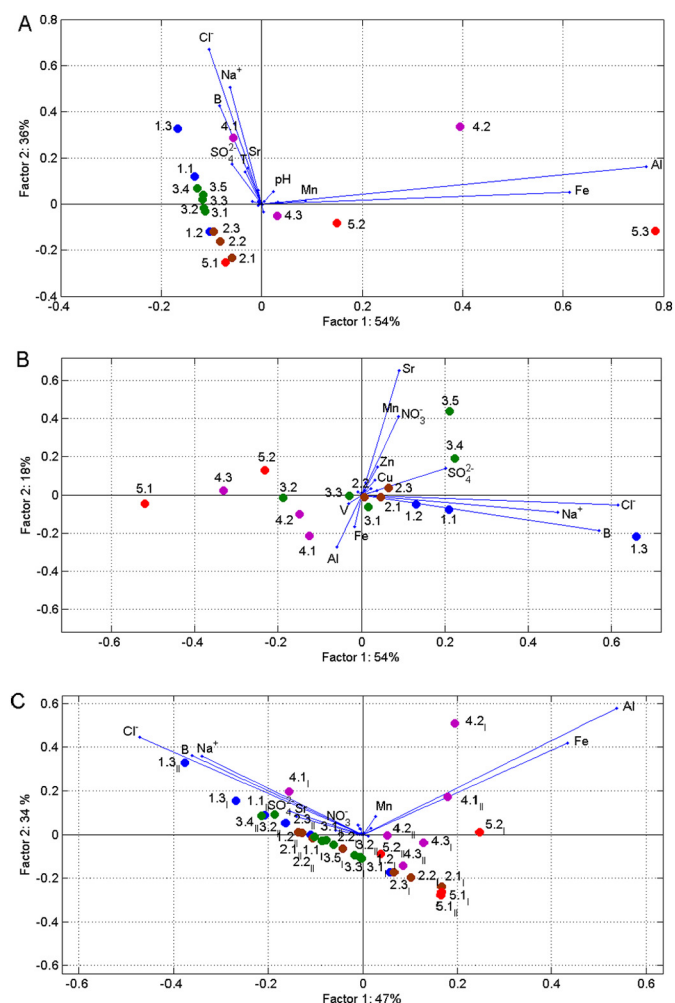
The direct influence of permafrost on water chemistry in the study area is difficult to recognise. The occurrence of discontinuous permafrost is confirmed by the occurrence of gelaquent soils confirmed by, among others (Simas et al., 2015). Under the progressive retreat of glaciers, periglacial conditions in the area of King George Island (Birkenmajer, 2002; Cook et al., 2005; Rückamp et al., 2011; Oliva and Ruiz-Fernández, 2016; Sobota et al., 2015; Pętlicki et al., 2017; Sziło and Bialik, 2017) represent a phase of geomorphological development as land surface becomes exposed and thus subjected to temporally variable thermal and precipitation conditions. At the same time, the influence of the ocean limits the spatial range of permafrost processes to altitudes above 10–20 m a.s.l. (Bockheim et al., 2013). According to Z. Zwoliński (2007) non-glaciated catchments partially fed by seasonal thawing of the active layer have a lower supply of suspended and dissolved matter than do catchments fed by glacier ablation waters. This is caused by the limited depth to which degraded material is washed out, which limits chemical denudation. It should also be emphasised that, due to the relatively short period for which the periglacial conditions have existed and the limited extent of vegetation cover on KGI, permafrost here is not the store of organic material that it is in mainland areas of Siberia or Canada. This can be seen in the fact that the differences between TOC values recorded in the non-glaciated and the glaciated catchments are only minor (Appendix A, Table A.3).

Total mineralisation and concentrations of most ions in the samples collected in areas I, II and III were higher in March, whereas in areas IV

Table 3

Values of Pearson's correlation coefficient (r) for total concentrations of investigated elements (selected metals, nonmetals and total organic carbon concentration). Strong and very strong correlations ($0.6 < |r| \leq 1$) are given in bold and red. Frames emphasise very strong correlations ($0.8 < |r| \leq 1$). Values of Pearson's correlation coefficients in the range ($0.6 < |r| \leq 1$) are statistically significant at $p < 0.05$.

	TOC	Li	Be	B	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Rb	Sr	Ag	Cd	Cs	Ba	La	Tl	Pb	Th	U
TOC	1																									
Li	0.139	1																								
Be	0.023	−0.062	1																							
B	**0.698**	0.417	−0.161	1																						
Al	−0.102	0.127	0.341	−0.098	1																					
V	−0.014	0.538	−0.150	0.305	0.159	1																				
Cr	0.194	−0.221	−0.030	0.137	−0.064	−0.130	1																			
Mn	−0.076	0.494	0.085	0.041	0.281	−0.085	−0.090	1																		
Fe	−0.084	0.058	0.330	−0.146	**0.982**	0.047	−0.043	0.287	1																	
Co	−0.089	0.491	−0.065	0.046	−0.107	−0.090	−0.026	**0.864**	−0.107	1																
Ni	0.523	0.216	−0.139	0.463	−0.068	0.030	0.182	0.256	−0.085	0.263	1															
Cu	0.244	0.280	0.080	0.117	−0.093	−0.230	−0.137	0.533	−0.078	0.413	0.422	1														
Zn	0.089	0.063	0.134	−0.135	0.008	−0.326	−0.082	0.513	0.027	0.367	0.271	**0.887**	1													
Ga	−0.014	0.507	−0.040	0.112	0.440	**0.680**	−0.116	0.019	0.341	−0.060	0.188	−0.171	−0.217	1												
As	0.407	0.277	−0.184	**0.605**	−0.229	0.323	−0.081	0.038	−0.249	0.175	0.315	0.203	−0.012	0.082	1											
Rb	**0.696**	0.462	−0.181	**0.733**	−0.141	−0.037	0.189	0.405	−0.132	0.393	**0.710**	0.535	0.264	0.053	0.430	1										
Sr	0.027	**0.744**	−0.228	0.382	−0.152	0.172	−0.168	0.506	−0.193	0.601	0.188	0.404	0.148	0.213	0.423	0.535	1									
Ag	0.319	−0.065	0.086	0.163	0.134	−0.221	0.259	0.074	0.152	−0.027	**0.533**	0.288	0.252	0.050	−0.022	0.388	−0.102	1								
Cd	0.008	0.230	0.128	0.098	0.094	−0.181	0.095	**0.705**	0.118	0.677	0.215	0.205	0.114	−0.225	0.037	0.339	0.238	0.118	1							
Cs	0.044	−0.050	0.252	−0.214	−0.189	−0.216	0.055	0.038	−0.154	0.095	−0.037	0.299	0.222	−0.197	−0.194	0.030	−0.137	0.168	0.190	1						
Ba	−0.112	**0.725**	0.019	0.100	0.295	0.477	−0.254	0.198	0.198	0.222	0.021	−0.022	−0.121	**0.684**	0.161	0.044	0.591	−0.145	−0.105	−0.177	1					
La	−0.015	−0.171	0.314	−0.254	0.543	−0.293	−0.007	0.202	**0.616**	−0.097	−0.043	0.173	0.183	−0.027	−0.395	−0.064	−0.332	0.233	0.135	0.447	−0.157	1				
Tl	0.218	0.272	−0.003	0.135	0.134	0.288	0.053	0.164	0.090	0.165	0.168	0.312	0.354	0.172	−0.034	0.198	0.028	0.288	−0.091	0.247	0.086	0.077	1			
Pb	0.487	0.164	0.101	0.348	−0.068	−0.279	0.216	0.343	−0.034	0.285	**0.751**	**0.661**	0.419	−0.086	0.194	**0.755**	0.276	**0.678**	0.336	0.320	−0.125	0.251	0.194	1		
Th	0.306	0.082	0.107	0.096	0.085	−0.170	0.006	0.260	0.106	0.095	0.279	**0.753**	**0.846**	−0.061	0.035	0.308	0.018	0.329	−0.169	0.255	−0.087	0.310	0.530	0.395	1	
U	0.044	0.591	−0.098	0.285	0.093	0.786	−0.108	−0.143	−0.026	−0.056	0.040	−0.262	−0.342	**0.836**	0.243	0.020	0.315	−0.163	−0.264	−0.127	0.720	−0.287	0.153	−0.258	−0.136	1

Fig. 5. PCA biplots for various data sets. Projection of environmental variables and cases (sampling points) on the plane of two principal components: A. data set for January; B. data set for March, C. entire data set (January and March).

Statistical analysis (Table 3) shows very strong correlations ($0.8 < |r| \leq 1$) between the following pairs of metals: Al and Fe (0.982), Co and Mn (0,864), and Zn and Cu (0.887). Such a correlation indicates that these metals may be of natural origin (Groeneweg and Beunk, 1992). Mozer et al. (2015) provided detailed major, trace and rare earth element concentrations of selected magmatic rock samples from the western shore of Admiralty Bay. Based on this analysis, contents of Al_2O_3 and Fe_2O_3 were in ranges 18.41–21.72% and 8.16–9.48%, respectively. The strong correlation between Al and Fe confirms the co-occurrence of these elements. Based on our result we can assume that Al and Fe are relatively quickly washed out of the uncovered morainic material, as is attested by their lower concentrations in non-glaciated catchments (areas I–III) (Appendix A, Table A.1). Moreover, based on our field observation, creeks in areas IV and V transport much more suspended material than creeks in areas I–III, and that may have intensified processes of Al and Fe chemical weathering (as has been mentioned above).

Volcanic rocks and soils of King George Island are relatively rich in Cu and Mn (Geoeneweg and Beunk 1992); however, Tatur (1989) pointed out the seabird origin of Cu, Zn and Sr. Hence, their presence in water samples is the result of geochemical weathering of volcanic rocks and ornithogenic soils, rather than the influence of anthropogenic activity (Lu et al., 2012). However, in order to check the sources of metals contamination for Arctowski station detailed geochemical analysis of soils is required. Calculation of the enrichment factor of potentially hazardous elements would definitely help to verify their natural concentration levels in the environment. Admittedly, in the case of Zn, Cu, Mn and Co, an anthropogenic impact on the concentration of these elements cannot be ruled out (particularly in the vicinity of the Arctowski station – areas I and II), as indicated on KGI by, among others Padeiro et al. (2016). Nevertheless, taking into account geological factors and the aforementioned considerable correlation between pairs of metals (Table 3), it can be assumed that the water is enriched in these elements largely due to processes of chemical denudation. Moreover, Hong et al. (2004) obtained the first reliable data on Cu, Zn and Cd in ancient Antarctic ice at Vostok Station. The authors indicate that Cu, Zn and Cd concentrations and fallout fluxes display very large natural variations. High values were obtained for the coldest climatic stages and much lower values during warm climatic stages. Hong et al. (2004) also pointed out that crustal dust was an important source of Cu and Zn during the coldest climatic stages, and volcanic emissions were probably an important source of Cd both in warm and in cold periods.

4.2. Other factors influencing water chemistry (atmospheric transport, biology and anthropogenic activity)

The location of the study area in Admiralty Bay displays a relatively high influence of marine aerosol on the chemistry of precipitation (Rachlewicz, 1997) and flowing water (Nędzarek et al., 2015).

Based on % nss SO_4^{2-} (Appendix A, Table A.4) we can observe that water in the highlands (2.1–2.3; 4.3 and 5.2) and in the mouth of Ornithologists Creek (3.4 and 3.5) had the highest % nss SO_4^{2-} (52.21–70.27%). This indicates a lower influence of marine aerosol and suggests atmospheric transport as a source of anthropogenic or biological (Giordano et al., 2016) nss SO_4^{2-}. Giordano et al. (2016) pointed out that, during springtime, increases in sulphate aerosol are observed and attributed them to biogenic sources (e.g. phytoplankton activity as the source of the aerosol). Based on the two obtained data series we do not observe any significant difference in % of nss SO_4^{2-} between January and March. That may suggest a relatively regular inflow of SO_4^{2-} throughout the austral summer. However, the observed relationship between the chemical composition of flowing water and short-term atmospheric episodes, such as rain and inflow of aerosols, calls for a detailed study based on more frequent sampling.

Animals living in the western shore of Admiralty Bay (Fig. 6h–l) may have a great impact on water chemistry characteristics. Seabirds in polar regions are considered an important means of transferring biogenic

and V we observed lower concentrations of ions (Table 2). This is most likely due to the difference in how the streams are fed at the beginning and towards the end of summer. In March, when there was no snow-melt, the streams in area I, II and III were fed mainly by groundwater, which caused a several-fold increase in the concentration of most ions (Table 2). Zwolicki et al. (2015) also note that, in the area of non-glaciated catchments (areas I–III), specific electrolytic conductivity SEC_{25} (SEC_{25} tends to illustrate the concentration of major ions) is lowest in January. Later on, conductivity tends to increase because of intensively leached bedrock-end sedimentary cover from within thawing ground. Streams in areas IV and V, on the other hand, are located at the forefield of the Sphinx and Baranowski glaciers and had been fed mainly by poorly mineralised water coming from underneath the glaciers, thus resulting in a different trend at this section. At the beginning of January, streams fed by melt- and glacier water had higher concentrations of major ions than at the beginning of March, when supply to streams was limited to glacier water.

As mentioned before, the study area is covered by andesite lavas, terrestrial basaltic andesite lavas, tuffs, andesite agglomerates, scorias and breccias (Birkenmajer, 2003). Furthermore, areas IV and V have been uncovered relatively recently as a result of glacier retreat, and consist of ground and marginal moraines. The mineralogical and fractional diversity in this area (Zwolicki et al., 2015) provides a unique opportunity to determine the influence of chemical weathering on water chemistry characteristics.

a weathering of rocks
b glacier moraines
c snow patches
d melting of glaciers
e water erosion during snow thawing
f wind transport
g mosses
h penguins
i ornithogenic soils
j antarctic fur seals
k weddell seals
l southern elephant seals

Fig. 6. Factors and processes influencing water chemistry characteristics.

compounds from the sea onto land, thus affecting the properties of soil and vegetation (Szopińska et al., 2016a). By extension, water found in the vicinity of penguin rookeries can be enriched with phosphorus and nitrogen (Nędzarek, 2008). Seabird guano and residues of ornithogenic soils' erosion can be deposited into lakes (Zhu et al., 2006) via being carried by melted ice and snow or being directly discharged (Hodson et al., 2010). Admittedly, marine birds and mammals inhabiting the study area are not the only source of biogenic elements. Attention should also be drawn to the distribution of vegetation in the area, as well as the presence of whale bones and macroalgae within the shore zones. Although whale bones and macroalgae indeed constitute point sources of cations and nutrients, the amounts released into the environment are negligible (Rakusa-Suszczewski and Nędzarek, 2002).We observed increased amounts of P and N in the chemical composition of water samples collected from Ornithologists Creek. Concentrations of NO_3^- have been detected up to 13.6 mg L^{-1} (Table 2). The Ornithologists Creek samples also showed the highest concentration of NH_4^+ (up to 0.258 mg L^{-1}). Similar results were obtained by Nędzarek et al. (2015) and the concentration values indicate the impact of penguin rookeries found nearby. Moreover, Zwolicki et al. (2014) emphasised that the concentration of nutrients and soil conductivity tends to decrease with the distance from bird colonies. Much lower concentrations in the range of 0.029–0.025 mg L^{-1} and 0.872–1.33 mg L^{-1} respectively for January and March have been recorded along Moss Creek. The area in question is located farther from the colonies and the orographic barrier effectively limits the

atmospheric transfer of these compounds and, hence, concentrations of NO_3^- are considerably lower. In the case of Moss Creek, the higher concentrations of biogenic substances may arise from the fact that the floor of the stream valley is largely covered by mosses (Fig. 2II). Vegetation distribution and pattern may play a significant role in enriching the water in these elements (Kappen and Schroeter, 2002). Concentrations of reactive phosphorus – PO_4^{3-} in Moss Creek ranged from 0.403 to 0.411 mg L^{-1} and from 0.368 to 410 mg L^{-1} in January and March, respectively. In Ornithologists Creek, concentrations of PO_4^{3-} ranged from 0.318 to 0.897 and 0.352 to 1.28 mg L^{-1} in January and March, respectively. Based on our two data series, we suggest that phosphates are likely leached from ornithogenic soils, rather than having been transferred atmospherically from the area of penguin rookeries, except for sample 3.5, which was taken from near a current nesting area and whose enrichment by PO_4^{3-} originated directly from penguin guano (Myrcha et al., 2013). The Penguin Ridge, located in the right-side of this catchment is a relict of penguin rookeries, built of ornithogenic soils with phosphatic substrate hidden by a cover of lichen and mosses (Tatur, 1989). These relict soils are enhanced with secondary phosphates. Their clay fraction is usually composed of secondary aluminium iron phosphates and the usual processes related to the penguin rookeries in the investigated area are: (1) formation of struvite (magnesium and ammonium phosphates), which is a mineral easily dissolved in water, (2) mineralisation of amorphous aluminium phosphate and apatite. Moreover, mineralisation of struvite depends on the co-occurrence of magnesium ions of marine origin and phosphorus and ammonia ions of ornithogenic origin (Tatur and Keck, 1990). Despite the phosphates, the ornithogenic soils are enriched in Cu, Zn and Sr which originates from penguin guano because of the high concentration of these trace elements in krill (Tatur, 1989). This is confirmed by the results obtained from Ornithologists Creek, because it is there that these trace elements have their highest concentrations of the waters from all the researched creeks (Appendix A, Table A.1). Furthermore, the mouth section (3.5) located near a penguin colony has the highest Cu, Zn and Sr contents of all analysed samples.

Concentrations of each biogenic substance (e.g. PO_4^{3-}, NO_3^-, NH_4^+) in the flowing waters of area IV (forefield of the Ecology glacier) and V (forefield of the Baranowski glacier), where flora is far less developed than in areas II and III, do not exceed 0.8 mgL^{-1}. The exception is point 4.3 (Seal Creek), where the concentration of NH_4^+ was 0.118 mgL^{-1}. This, however, is likely due to the presence of elephant seals at the nearby beach. The forefields of glaciers, being newly established forms of terrain, can be regarded as an excellent reference point for comparison with areas I–III. Observation of changing hydrochemical conditions may help us verify the processes related to, for instance, primary succession in these areas.

Several studies based on environmental monitoring results are extensively discussed in the context of pollution levels in Antarctica in Szopińska et al. (2016a). Furthermore, Tin et al. (2009) highlighted that the most commonly found contaminants are those related to accidental fuel spills—potentially toxic elements (arsenic, cadmium, copper, lead, mercury and zinc). They can be also emitted into the environment through the use of petrol engines (Mishra et al., 2004). However, when addressing comprehensively the issue of heavy metals being treated as pollution in Antarctica, it is also very important to become familiar with natural enrichment of heavy metals in this environment. One cannot ignore the geochemical characteristics of a given area, including metals transported from the terrestrial to the marine environment as particulate or soluble fraction (Vodopivez et al., 2015), because heavy metals found in the environment can also be of natural origin (volcanic or geological sources) (Szopińska et al., 2016a). Hence, we do agree with Nędzarek et al. (2014) and Lu et al. (2012) that special attention should be drawn to the differentiation between natural and anthropogenic sources of heavy metals, especially in the area of King George Island, where anthropogenic activity is greater than in other areas of the Antarctic due to (1) the large number of scientific stations, and (2) relatively

easy access to the island, which has seen an increase in tourist traffic in the recent years (Harcha, 2006).

Natural enrichment of trace elements in the water depends upon, inter alia the nature of rocks, climatic factors, type and extent of mineralisation and water pH. Ficklin proposed an idea to classify water against the relationship between total base metal (Zn, Cu, Pb, Cd, Ni, Co) content and water pH (Naseem et al., 2014). According to the Ficklin diagram (Fig. 4) in the majority of studied samples, total base concentration can be classified as low and, as such, is independent of pH. Although the Ficklin diagram was originally devised to monitor the quality of mine water, we decided to apply this concept to the Antarctic fresh water samples, as it allowed us to verify the potential risk to the environment of heavy metal exposure. Despite the fact that chemical weathering of metals from water is believed to be independent of pH (Naseem et al., 2014), we may observe this phenomenon in Fig. 4. Toro et al. (2007) pointed out that the Antarctic flowing waters have a low buffer capacity, which means that pH can increase even with a minor rise in primary production. Thus, we did not observe any significant difference in total base metal content related to changes in pH. Slightly higher concentrations of heavy metals were recorded in the mouth section of Ornithologists Creek and in the sample collected at the Baranowski glacier forefield (Seal Creek), ranging from 11.7 to 25.7 µg L^{-1}. In both cases the highest concentrations of selected metals are observed in January, in the end phase of snow melt. It is of importance that, due to variable topography, snow melt takes a long time and the process spans the summer, when the last patches of snow melt on the slopes least exposed to sun. This means that the mouth section of the stream tends to accumulate the metals in question from both the spring melt and soil leaching. In the sample collected from Ornithologists Creek, concentrations are slightly higher than in the remaining sampling points, with Σ(Zn, Cu, Pb, Cd, Ni, Co) <6 µg L^{-1}. This is due to the location of the point in the mouth section of the stream, which may result in accumulation of metals.

When discussing anthropogenic influences on polar environments, it is important to investigate concentrations of Pb in flowing water. Combustion engines are believed to be the primary source of Pb in Admiralty Bay (Dias da Cunha et al., 2009). Compared to the data from 2005 presented by Nędzarek et al. (2014), we observed no increased concentration of Pb in summer 2016. In most samples the recorded concentration was <LOD, the exception being point 1.3 (outflow from the water reservoir at the Arctowski station) where it was 0.03 µg L^{-1} (= LOD). In 2005 the range for Pb concentration in the Petrified Forest Creek was 6.05–36.5 µg L^{-1} (Nędzarek et al., 2014). Thus, it appears that, over the last decade, Pb emission decreased over a-hundred-fold. Moreover, Pb concentrations are considerably lower than in other areas of the South Shetland Islands, e.g. Pb concentration in fresh water samples on Deception Island was 0.049 µg L^{-1} (Mao de Ferro et al., 2013) and in several lagoons of King George Island, was in the range <0.1–0.4 µg L^{-1} (Préndez and Carrasco, 2003). Nevertheless, combustion engine emission is regarded as a point source of pollution and the recorded drop in Pb concentration in water may be seasonal. Furthermore, Amaro et al. (2015) pointed out that oil spills result in an increase in Pb concentrations. Therefore, it is recommended that concentrations of heavy metals, and Pb in particular, be continuously monitored. Taking into consideration that even a minor increase in concentration of heavy metals in polar environments may considerably affect the development of fauna and flora in the Antarctic (Bargagli, 2008), there is a need to design a diagram of heavy metal concentrations that would differentiate the potential sources of heavy metal emission to the environment, dividing them into anthropogenic (aerosols, impact of research stations) and natural (chemical leaching, weathering) factors. For this reason it is suggested that data regarding concentration levels of individual heavy metals in various environments (soil, flowing and still water, ice, precipitation) be gathered over a period of at least several years.

4.3. Major factors affecting water chemistry in the entire study area – PCA results analysis

Multivariate data set analysis allowed us to identify the primary groups of chemical variables that shape water chemistry in the study area: (1) Na^+, Cl^- and B and (2) Al and Fe. The first group is clearly associated with the influence of marine aerosols on water chemistry; the second is related to the chemical weathering of bedrock end sedimentary cover. Although the origin of Na^+ and Cl^- from marine aerosol is quite clear, one may not neglect the significance of boron in individual PCs. Boron is a volatile element accompanying volcanic activity (Katalin et al., 2007), which is known to be the primary source of this element in both the atmosphere and the oceans. Rock weathering and anthropogenic activity (e.g. burning of fossil fuel and agricultural fires) represent only a minor contribution to the circulation of boron between the atmosphere and the marine environment (Kot, 2015). Moreover, the influence of volcanic activity can be local, e.g. Deception Island, and global, e.g. inflow of volcanic dust from Patagonia reported by Lee et al. (2004).

The PCA of the January data set (Fig. 5A) shows that waters from Petrified Forest Creek and Ornithologists Creek are greatly influenced by marine aerosol. Furthermore, samples taken in the forefield of the Sphinx and Baranowski Glaciers are shaped by intense weathering processes, the exceptions being the sample collected from Sphinx Creek-1, which indicates a significant influence of marine aerosols, and the sample of subglacial water from Baranowski Glacier, where none of the factors appear to dominate. Water from Moss Creek has a different chemical characteristic. It may be associated with the location of the creek in non-glaciated areas which are covered by a moss carpet (Fig. 2). On the other hand, PCA of the March data set (Fig. 5B) shows a more complex contribution of these factors in the shaping of water chemistry. For instance, samples taken from Ornithologists Creek indicate that the mouth section of the stream is influenced by the presence of Antarctic birds (e.g. south polar skua; Adélie, gentoo and chinstrap penguins) and mammals (e.g. southern elephant seals and Weddell seals) (occurrence of NO_3^-). The joint PCA for both series presented in Fig. 5C clearly shows that for most points the share of chemical factor in both months is stable; for example, point 1.3 (outflow of Petrified Forest Creek) is under the significant influence of marine aerosols, whereas point 5.1 represents data from the glacier outflow, where the influence of Al and Fe is considerable. In contrast, points 2.2 (Moss Creek) and 4.1 (Sphinx-1 Creek), where samples were taken from small creeks, were found to be considerably affected by either marine aerosol or local conditions.

5. Conclusion

The comprehensive hydrochemical analysis of freshwater samples taken from the western shore of Admiralty Bay in summer 2016 helped to conclude following:

(1) in the studied area there is a visible difference in water chemistry between new periglacial zones (areas IV–V) and those areas uncovered by the glaciers in the more distant past (areas I–III). Based on total measured contents of mineral constituents, there is a visible difference in the feeding of creeks in these areas at the beginning and by the end of the austral summer (differences are caused by the various inputs of glacier meltwater and snowmelt, and varied intensification of weathering processes);

(2) PCA analysis help to differentiate two groups of chemical variables shaping water chemistry, (I) the first, associated with marine aerosol influence (presence of Na^+, Cl^- and B) and (II) the second, associated with chemical weathering processes (presence of Al and Fe).

(3) elements such as Rb, Cu, Mn, Al, Fe are considered to be of natural origin. However, natural concentration levels of some potentially

hazardous elements (e.g., Zn, Cu, Pb, Cd, Ni and Co) need to be verified (e.g., by calculating enrichment factor from soil analysis results);

(4) nss SO_4^{2-} analysis (average % of nss SO_4^{2-} ~46%) indicates uniform inflow of SO_4^{2-} from biological and anthropogenic sources together with marine aerosol;

(5) water formation at Ornithologists and Moss Creeks are strongly under the influence of Antarctic biota e.g. seabirds, lichens and mosses (increase of PO_4^{3-}, NO_3^-, NH_4^+, Zn, Cu and Sr concentrations);

(6) the permafrost influence on water chemistry characteristic is difficult to confirm, because the relatively narrow ice-free zones are under the influence of glacier and snow melting, as well as marine factors. Moreover, the relatively short existence of the periglacial forms in the new ice-free area indicates the not very significant difference between TOC concentration in waters and indicates that permafrost does not constitute a store of organic matter;

(7) taking into account the permanent activity of the Arctowski station, it is suggested that monitoring of concentration levels of individual heavy metals in various environments (soil, flowing and still water, ice, precipitation) should be undertaken to observe any direct anthropogenic influence on this area.

Taking into consideration that the entirety of the South Shetland Islands displays certain common features, some of the data can potentially be used not only in relation to Admiralty Bay, but also for other areas of Maritime Antarctica.

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References

Amaro, E., Padeiro, A., Mão de Ferro, A., Mota, A.M., Leppe, M., Verkulich, S., Hughes, K.A., Peter, H.-U., Canário, J., 2015. Assessing trace element contamination in Fildes Peninsula (King George Island) and Ardley Island, Antarctic. Mar. Pollut. Bull. 97, 523–527.

Anderson, S.P., Drever, J.I., Frost, C.D., Holden, P., 2000. Chemical weathering in the foreland of a retreating glacier. Geochim. Cosmochim. Acta 64 (7), 1173–1189.

Bargagli, R., 2008. Environmental contamination in Antarctic ecosystems. Sci. Total Environ. 400, 212–226.

Birkenmajer, K., 2002. Retreat of ecology glacier, Admiralty Bay, King George Island (South Shetland Islands, West Antarctica) 1956–2001. Bull. Acad. Pol. Sci. 50, 15–29.

Birkenmajer, K., 2003. Admiralty Bay, King George Island (South Shetland Islands, West Antarctica): a geological monograph. Stud. Geol. Pol. 120 (14), 5–73.

Birkenmajer, K., Francalancp, L., Peccerill, A., 1991. Petrological and geochemical constraints on the genesis of Mesozoic-Cenozoic magmatism of King George Island, South Shetland Islands, Antarctica. Antarct. Sci. 3 (3), 293–308.

Bockheim, J., Vieira, G., Ramos, M., López-Martínez, J., Serrano, E., Guglielmin, M., Wilhelm, K., Nieuwendam, A., 2013. Climate warming and permafrost dynamics in the Antarctic Peninsula region. Glob. Planet. Chang. 100, 215–223.

Brown, G.H., 2002. Glacier meltwater hydrochemistry. Appl. Geochem. 17, 855–883.

Cook, A., Fox, A., Vaughan, D., Ferrigno, J., 2005. Retreating glacier fronts on the Antarctic Peninsula over the past half century. Science 308, 541–544.

Dias da Cunha, K., Medeiros, G., Leal, M.A., Lima, C., Dalia, K.C., Barros Leite, C.V., 2009. Aerosols in King George Island (Antarctic Peninsula) using PIXE and alpha spectrometry. International Nuclear Atlantic Conference, Rio de Janeiro, Brazil, September 27 to October 2.

Faure, G., 2001. Chemical properties and isotopic systematic. Origin of Igneous Rocks. The Isotopic Evidence, p. 1.

Fountain, A.G., Levy, J.S., Gooseff, M.N., Van Horn, D., 2014. The McMurdo Dry Valleys: A landscape on the threshold of change. Geomorphology 225, 25–35.

Giordano, M.R., Kalnajs, L.E., Avery, A., Goetz, J.D., Davis, S.M., DeCarlo, P.F., 2016. A missing source of aerosols in Antarctica – beyond long-range transport, phytoplankton, and photochemistry. Atmos. Chem. Phys. Discuss. http://dx.doi.org/10.5194/acp-2016-606.

Groeneweg, W.J., Beunk, F.F., 1992. The petrography and geochemistry of the King George Island supergroup and Admiralty Bay group volcanics, South Shetland Islands. In: Lopez-Martinez, J. (Ed.), Geologia de la Antartida Occidental. III Congreso Geologico de Espana y VIII Congresso Latinoamericano de Geologia, Salamanca, Espana, pp. 46–60.

Guglielmin, M., Vieira, G., 2014. Permafrost and periglacial research in Antarctica: New results and perspectives. Geomorphology 225, 1–3.

Harcha, J.Y., 2006. Tourism in Antarctica: History, Current Challenges and Proposals for Regulation. LLM Theses and Essays. Paper 74. http://digitalcommons.law.uga.edu/stu_llm/74 (Accessed: 10.01.2017).

Hawes, I., Brazier, P., 1991. Freshwater stream ecosystems of James Ross Island, Antarctica. Antarct. Sci. 3, 265–271.

Hodson, A., Heaton, T., Langford, H., Newsham, K., 2010. Chemical weathering and solute export by meltwater in a maritime Antarctic glacier basin. Biogeochemistry 98, 9–27.

Hong, S., Boutron, C.F., Gabrielli, P., Barbante, C., Ferrari, C.P., Petit, J.R., Lee, K., Lipenkov, V.Y., 2004. Past natural changes in Cu, Zn and Cd in Vostok Antarctic ice dated back to the penultimate interglacial period. Geophys. Res. Lett. 31, L20111. http://dx.doi.org/10.1029/2004GL021075.

Juchnowicz-Bierbasz, M., 1999. Year-round changes of nutrients in fresh water bodies near Arctowski Station (South Shetland Islands, Antarctica). Pol. Polar Res. 20, 243–258.

Kallenborn, R., Breivik, K., Eckhardt, S., Lunder, C.R., Manø, S., Schlabach, M., Stohl, A., 2013. Longterm monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. Atmos. Chem. Phys. Discuss. 13, 6219–6246.

Kappen, L., Schroeter, B., 2002. Plants and Lichens in the Antarctic, their way of life and their relevance to soil formation. In: Beyer, L., Bölter, M. (Eds.), Geoecology of Antarctic Ice-Free Coastal Landscapes, pp. 343–345.

Katalin, G., Károly, N., Ulrike, M., Nelson, E., Zsolt, V., 2007. Boron concentrations of volcanic fields in different geotectonic settings. J. Volcanol. Geotherm. Res. 159, 70–84.

Kejna, M., 1999. Air Temperature in the Admiralty Bay Region (King George Island, Antarctica) in the Period 1977–1996 According to Meteorological Data from the Arctowski Station. 128. Wydawnictwo Uniwersytetu Mikołaja Kopernika, Toruń.

Kejna, M., Araźny, A., Sobota, I., 2013a. Climatic change on King George Island in the years 1948–2011. Pol. Polar Res. 34 (2), 213–235.

Kejna, M., Araźny, A., Sobota, I., Piszczek, J., Łabno, R., 2013b. Meteorological conditions at the Arctowski station (King George Island, Antarctic) in 2012. Probl. Klimatologii Polarnej 23, 43–56 (In Polish with English abstract).

Kot, F.S., 2015. Boron in the environment. Boron Separation Processes ISBN 978-0-444-63454-2, http://dx.doi.org/10.1016/B978-0-444-63454-2.00001-0 [Accessed: 10.01.2017].

Lee, Y.I., Lim, H.S., Yoon, I., 2004. Geochemistry of soils of King George Island, South Shetland Islands, West Antarctica: implications for pedogenesis in cold polar regions. Geochim. Cosmochim. Acta 68 (21), 4319–4333.

López-Martínez, J., Serrano, E., Schmid, T., Mink, S., Linés, C., 2012. Periglacial processes and landforms in the South Shetland Islands (northern Antarctic Peninsula region). Geomorphology 155–156, 62–79.

Lu, Z., Cai, M., Wang, J., Yang, H., He, J., 2012. Baseline values for metals in soils on Fildes Peninsula, King George Island, Antarctica: the extent of anthropogenic pollution. Environ. Monit. Assess. 184, 7013–7021.

Mao de Ferro, A., Mota, A.M., Canario, J., 2013. Sources and transport of As, Cu, Cd and Pb in the environmental compartments of Deception Island, Antarctica. Mar. Pollut. Bull. 77, 341–348.

Mink, S., López-Martínez, J., Maestro, A., Garrote, J., Ortega, J.A., Serrano, E., Durán, J.J., Schmid, T., 2014. Insights into deglaciation of the largest ice-free area in the South Shetland Islands (Antarctica) from quantitative analysis of the drainage system. Geomorphology 225, 4–24.

Mishra, V.K., Kim, K.-H., Hong, S., Lee, K., 2004. Aerosol composition and its sources at the King Sejong Station, Antarctic peninsula. Atmos. Environ. 38, 4069–4084.

Mozer, A., Pécskay, Z., Krajewski, K.P., 2015. Eocene age of the Baranowski Glacier Group at Red Hill, King George Island, West Antarctica. Pol. Polar Res. 36 (4), 307–324.

Mulvaney, R., Abram, N.J., Hindmarsh, R.C.A., Arrowsmith, C., Fleet, L., Triest, J., Sime, L.C., Alemany, O., Foord, S., 2012. Recent Antarctic Peninsula warming relative to Holocene climate and ice-shelf history. Nature 489, 141–145.

Myrcha, A., Pietr, S.J., Tatur, A., 2013. The role of pygoscelid penguin rookeries in nutrient cycles at Admiralty Bay, King George Island. In: Siegfried, W.R., Condy, P.R., Laws, R.M. (Eds.), Antarctic Nutrient Cycles and Food Webs. Springer Science & Business Media, pp. 156–162.

Naseem, S., Hamza, S., Nawaz-ul-Huda, S., Bashir, E., Ul-Haq, Q., 2014. Geochemistry of Cd in groundwater of Winder, Balochistan and suspected health problems. Environ. Earth Sci. 71, 1683–1690.

Nędzarek, A., 2008. Sources, diversity and circulation of biogenic compounds in Admiralty Bay, King George Island, Antarctica. Antarct. Sci. 20 (2), 135–145.

Nędzarek, A., Pociecha, A., 2010. Limnological characterization of freshwater systems of the Thomas Point Oasis (Admiralty Bay, King George Island, West Antarctica). Polar Sci. 4, 457–467.

Nędzarek, A., Tórz, A., Drost, A., 2014. Selected elements in surface waters of Antarctica and their relations with the natural environment. Polar Res. 33:21417. http://dx.doi.org/10.3402/polar.v33.21417.

Nędzarek, A., Tórz, A., Podlasińska, J., 2015. Ionic composition of terrestrial surface waters in Maritime Antarctic and the processes involved in formation. Antarct. Sci. 27 (2), 150–161.

Oliva, M., Ruiz-Fernández, J., 2015. Coupling patterns between para-glacial and permafrost degradation responses in Antarctica. Earth Surf. Process. Landf. http://dx.doi.org/10.1002/esp.3716.

Oliva, M., Ruiz-Fernández, J., 2016. Geomorphological processes and frozen ground conditions in Elephant Point (Livingston Island, South Shetland Islands, Antarctica). Geomorphology http://dx.doi.org/10.1016/j.geomorph.2016.01.020.

Padeiro, A., Amaro, E., dos Santos, M.M.C., Araújo, M.F., Gomes, S.S., Leppe, M., Verkulich, S., Hughes, K.A., Peter, H.-U., Canário, J., 2016. Trace element contamination and availability in the Fildes Peninsula, King George Island, Antarctica. J. Article Environ. Sci.: Processes Impacts 18, 648–657.

Paulo, A., Rubinowski, Z., 1987. Pyrite mineralization on King George Island (South Shetland Islands Antarctica): its distribution and origin. Stud. Geol. Pol. XC, 38–85.

Pętlicki, M., Sziło, J., MacDonell, S., Vivero, S., Bialik, R.J., 2017. Recent deceleration of the ice elevation change of ecology glacier (King George Island, Antarctica). Remote Sens. 9, 520.

Préndez, M., Carrasco, A.M., 2003. Elemental composition of surface waters in the Antarctic Peninsula and interactions with the environment. Environ. Geochem. Health 25, 347.

Pudełko, R., 2008. Two new topographic maps for sites of scientific interest on King George Island, West Antarctica. Pol. Polar Res. 29 (3), 291–297.

Rachlewicz, G., 1997. Mid-winter thawing in the vicinity of Arctowski Station, King George Island. Pol. Polar Res. 18 (1), 15–24.

Rakusa-Suszczewski, S., Nędzarek, A., 2002. Whale bones and acroalgae as source of nutrients and cations in the nearshore geosystem of Admiralty Bay (King George Island, Antarctica). Pol. J. Ecol. 50 (3), 389–396.

Rückamp, M., Braun, M., Suckro, S., Blindow, N., 2011. Observed glacial changes on the King George Island ice cap, Antarctica, in the last decade. Glob. Planet. Chang. 79, 99–109.

Schaefer, C.E.G.R., Santana, R.M., Simas, F.N.B., Francelino, M.R., Filho, E.I.F., Albuquerque, M.A., Calijuri, M.L., 2007. Geoenvironments from the vicinity of Arctowski Station, Admiralty Bay, King George Island, Antarctica: vulnerability and valuation asessment, U.S. Geological Survey and The National Academies. Short Research Paper 015 http://dx.doi.org/10.3133/of2007-1047.srp015.

Simas, F.N.B., Schaefer, C.E.G.R., Michel, R.F.M., Francelino, M.R., Bockheim, J.G., 2015. Soils of the South Orkney and South Shetland Islands, Antarctica. In: Bockheim, J.G. (Ed.), The Soils of Antarctica. Springer, Switzerland, pp. 227–273.

Simões, J.C., Bremer, U.F., Aquino, F.E., Ferron, F.A., 1999. Morphology and variations of glacial drainage basins in the King George Island ice field, Antarctica. Ann. Glaciol. 29, 220–224.

Sobota, I., Kejna, M., Araźny, A., 2015. Short-term mass changes and retreat of the Ecology and Sphinx glacier system, King George Island, Antarctic Peninsula. Antarct. Sci. 27 (5), 500–510.

Stumm, W., Morgan, J., 1996. Aquatic chemistry. 3rd ed. John Wiley & Sons, New York.

Sziło, J., Bialik, R., 2017. Bedload transport in two creeks at the ice-free area of the Baranowski Glacier (King George Island, West Antarctica). Pol. Polar Res. 38 (1), 21–39.

Szopińska, M., Namieśnik, J., Polkowska, Ż., 2016a. How important is research on pollution levels in Antarctica? Historical approach, difficulties and current trends. Rev. Environ. Contam. Toxicol. 239, 79–156.

Szopińska, M., Szumińska, D., Polkowska, D., Machowiak, K., Lehmann, S., Chmiel, S., 2016b. The chemistry of river-lake systems in the context of permafrost occurrence (Mongolia, Valley of the Lakes) part I. Analysis of ions and trace metals concentrations. Sediment. Geol. 340, 74–83.

Tatur, A., 1989. Ornithogenic soils of the maritime Antarctic. Pol. Polar Res. 10, 481–532.

Tatur, A., Keck, A., 1990. Phosphates in ornithogenic soils of the maritime Antarctic. Proc. NIPR Symp. Polar Biol. 3, 133–150.

Tin, T., Fleming, Z.L., Hughes, K.A., Ainley, D.G., Convey, P., Moreno, C.A., Pfeiffer, S., Scott, J., Snape, I., 2009. Impacts of local human activities on the Antarctic environment. Antarct. Sci. 21 (1), 3–33.

Toro, M., Camacho, A., Rochera, C., Rico, E., Bañon, M., Fernandez-Valiente, E., Marco, E., Justel, A., Avendano, M.C., Ariosa, Y., Vincent, W.F., Quesada, A., 2007. Limnological characteristics of the freshwater ecosystems of Byers Peninsula, Livingston Island, in Maritime Antarctic. Polar Biol. 30, 635–649.

Tranter, M., Wadham, J.L., 2014. Geochemical weathering in glacial and proglacial environments, treatise on geochemistry (second edition). Reference Module in Earth Systems and Environmental Sciences. 7, pp. 157–173.

Turner, J., Colwell, S.R., Marshall, G.J., Lachlan-Cope, T.A., Carleton, A.M., Jones, P.D., Lagun, V., Reid, P.A., Lagovkin, S., 2005. Antarctic climate change during the last 50 years. Int. J. Climatol. 25, 279–294.

Vaughan, D.G., Marshall, G.J., Connolley, W.M., Parkinson, C., Mulvaney, R., Hodgson, D.A., King, J.C., Pudsey, C.J., Turner, J., 2003. Recent rapid regional climate warming on the Antarctic Peninsula. Climate Change 60, 243–274.

Vieira, G., López-Martínez, J., Serrano, E., Ramos, M., 2008. Climate change and permafrost degradation. Geomorphological evidence from Deception and Livingston islands, maritime Antarctic. In: Kane, D.L., Hindel, K.M. (Eds.), Proceedings Ninth International Conference on Permafrost. 2. Institute of Northern Engineering, University of Alaska, Fairbanks, pp. 1839–1844.

Vodopivez, C., Curtosi, A., Villaamil, E., Smichowski, P., Pelletier, E., Mac, W.P., 2015. Metals in sediments and soft tissues of the Antarctic clam Laternula elliptica: more evidence as a possible biomonitor of coastal marine pollution at high latitudes. Sci. Total Environ. 502, 375–384.

Waldner, P.A., Burch, H., 1996. Chemistry of Snow Melt Runoff. WSL, Swiss Federal Institute for Forest, Snow and Landscape Research http://www.wsl.ch/info/mitarbeitende/waldner/pdf/Waldner1996_SnowMeltChemistry.pdf.

Wojtuń, B., Fabiszewski, J., 1999. Chemical properties of freshwater environment at the Admiralty Bay region (West Antarctica). Polish Polar Studies XXVI Polar Symposium, Lublin, June 1999, pp. 393–399.

Zhu, R.B., Sun, L.G., Kong, D.M., Geng, J.J., Wang, N., Wang, Q., Wang, X.R., 2006. Matrix-bound phosphine in Antarctic biosphere. Chemosphere 64 (1), 1429–1435.

Zwolicki, A., Barcikowski, M., Barcikowski, A., Cymerski, M., Stempniewicz, L, Convey, P., 2014. Seabird colony effects on soil properties and vegetation zonation patterns on King George Island, Maritime Antarctic. Polar Biol. http://dx.doi.org/10.1007/s00300-015-1730-z.

Zwolicki, A., Barcikowski, M., Barcikowski, A., Cymerski, M., Stempniewicz, L, Convey, P., 2015. Seabird colony effects on soil properties and vegetation zonation patterns on King George Island, Maritime Antarctic. Polar Biol. 38 (10), 1645–1655.

Zwoliński, Z., 2007. Mobilność materii mineralnej na obszarach paraglacjalnych, Króla Jerzego,Wyspa, Zachodnia, Antarktyka. Wydawnictwo Naukowe UAM, Poznań (In Polishwith English abstract).

Zwoliński, Z., Kejna, M., Rachlewicz, G., Sobota, I., Szpikowski, J., 2016. Solute and sedimentary fluxes on King George Island. In: Beylich, A.A., Dixon, J., Zwoliński, Z. (Eds.), Source-to-Sink Fluxes in Undisturbed Cold Environments. Cambridge University Press, pp. 213–237.