

#### RESEARCH/REVIEW ARTICLE

# Selected elements in surface waters of Antarctica and their relations with the natural environment

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#### Keywords

Antarctic surface waters; total and dissolved elements; baseline elements values; anthropogenic metal contamination.

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# Abstract

The aim of the study was to specify the concentration of selected chemical elements in surface waters of King George Island, off the western coast of the Antarctic Peninsula. The research encompassed six streams, a lake and an artificial water reservoir located on the western coast of Admiralty Bay. Measured hydrochemical parameters included pH, conductivity, total dissolved solids (TDS), and total and dissolved forms elements such as Al, Co, Ni, Cu, Zn, Cd, Pb, Mn, Fe, As and Se. The values of pH, conductivity and TDS had the following ranges: 6.09-8.21,  $6.0-875~\mu S$  cm  $^{-1}$  and 7.0-975 mg/L, respectively, and were typical for surface waters of Antarctica. Wide disparities were discovered regarding concentrations of the investigated elements, ranging from  $<0.01 \mu g/L$  for Cd to 510  $\mu g/L$  for Fe, and differing from one water body to another. The investigated elements are discussed with reference to environmental conditions and anthropogenic factors. Concentrations of total and dissolved forms of elements are considered in connection with the composition of soil in their surroundings and with atmospheric deposition, mostly such as that took place locally. The increased levels of Pb and Zn concentrations in the immediate proximity of a research station suggested anthropogenic contamination.

To access the supplementary material for this article, please see Supplementary files under Article Tools online.

One of the results of human impact is a change in the concentrations of trace metals in surface waters of the Earth; therefore it is advisable to conduct research in parts of the world located far from industrialized and populated areas. The isolation of Antarctica provides an opportunity to study surface waters in their original state and to treat them as a reference point with respect to other areas of the Earth (Préndez & Carrasco 2003). It is a matter of particular importance to recognize the qualitative composition of surface waters in regions characterized by progressive deglaciation. In Antarctica, the Antarctic Peninsula is such a region. For four decades the results of climate warming, including melting glaciers and the occurrence of areas free from ice both alongside the coast and inland, have been observed there (Martianov & Rakusa-Suszczewski 1990; King 1994; Skvarca et al. 1998; Birkenmajer 2002; Cook et al. 2005).

An especially important research area is King George Island, one of the South Shetland Islands. It is one of the most populated areas of the maritime Antarctica, where deglaciation processes have been observed since the 1970s (Martianov & Rakusa-Suszczewski 1990; Birkenmajer 2002). This provides an opportunity for conducting research both in an environment subject to heavy human impact (e.g., Fildes Peninsula) and in an environment subject to almost no human impact.

The aim of our study was to discuss the composition of selected elements occurring in surface waters of the western coast of Admiralty Bay, King George Island, with respect to basic hydrochemical indicators (pH, conductivity, dissolved solids) and to focus on mechanisms determining the presence of the elements in suspended and dissolved fractions. The problem of origin of the studied elements from natural and anthropogenic

sources was considered, taking into account air pollutants brought from the island and/or neighbouring continents by the wind.

#### Material and methods

The studied surface water bodies are located on the western coast of Admiralty Bay (King George Island, South Shetland Islands, Antarctic Peninsula; Fig. 1). Admiralty Bay is situated in the sub-polar climatic zone, characterized by strong winds, high air humidity, total precipitation exceeding 505 mm, striking changeability of daily weather and considerable fluctuations in air temperature—from -32 to  $+16^{\circ}$ C (Kratke & Wielbińska 1981; Styszyńska 1990; Marsz & Styszyńska 2000). Since 1977, an all-year Polish station named after H. Arctowski has functioned in the area. During this period, progressive deglaciation was observed off the coast of Admiralty Bay, north of Ecology Glacier (the area covered by this glacier in 1979 is shown in Fig. 1).

The research encompassed six streams: Petrified Forest Creek (PFC), Ornithologists Creek (OC), Czech Creek (CC), a stream running along the border of Ecology Glacier (EG), Vanishing Creek (VC), a stream running across the Wróbel Valley (WV) and Lake Wujka (LW), as well as an artificial drinking water reservoir (DWR) which belonged to the research station (Fig. 1).

Water samples were collected from the sources and mouths of streams, and in the case of OC additional samples were collected midstream. As for LW and DWR, samples were collected from the central part of the reservoirs at a depth of 20 cm below the water surface. Samples were collected between January and March 2005.

We used procedures of water sample collection, storage and analysis that minimized the possibility of sample contamination. Polyethylene bottles and their caps utilized for storing samples had been cleaned with 2%  $HNO_3$ , rinsed with MilliQ purified water (18.2 M $\Omega$ ) and dried at a temperature of 30-35°C. The dissolved fractions were analysed in 500 mL samples filtered through a 0.45 µm polypropylene membrane that had been purified with ultrapure water and 150 mL samples of tested water. Water samples (both filtered and unfiltered) were preserved by adding 2 mL of HNO<sub>3</sub> to lower the pH value below 2, frozen and transported to Poland, where they were subject to further analysis according to the methodology specified by the American Public Health Association (APHA 1995). In all cases, Al, Co, Ni, Cu, Zn, Cd, Pb, Mn, Fe, As and Se were quantified by an Elan DRC-e inductively coupled plasma-mass spectrometer (ICP-MS; Perkin Elmer, Waltham, MA, USA). All analyses were carried out in duplicate. Certified model solutions produced by Tusnovics Instruments (Krakow, Poland) were used to assess measurement precision and construct

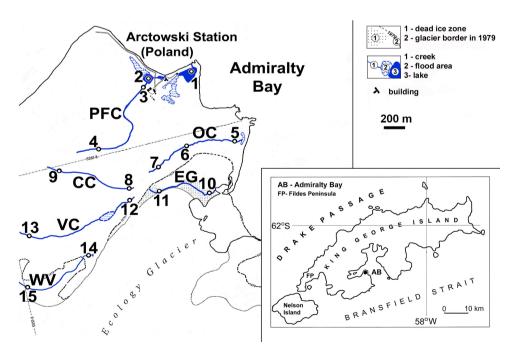


Fig. 1 Location of the research area on the western coast of Admiralty Bay featuring sampling sites (nos. 1–15) where surface water samples were collected: 1 Lake Wujka (LW); 2 drinking water reservoir (DWR); 3, 4 Petrified Forest Creek (PFC); 5, 6, 7 Ornithologists Creek (OC); 8, 9 Czech Creek (CC); 10, 11 stream flowing along the border of Ecology Glacier (EG); 12, 13 Vanishing Creek (VC); 14, 15 stream flowing across the Wróbel Valley (WV).

calibration curves. Spectral interferences were corrected with the help of Merck's (Whitehouse Station, NJ, USA) internal model: 103Rh (10 mg/L Rh[NO<sub>3</sub>]<sub>3</sub> in HNO<sub>3</sub> 2-3%). The precision of the analytical procedures (calculated as standard deviations of triplicates) was higher than 10%. Detection levels (in ng/L) amounted to: Al 0.09; Co 1.0; Ni 1.2; Cu 0.5; Zn 0.3; Cd 0.08; Pb 0.06; Mn 0.78; Fe 0.20; As 0.9; and Se 1. Prior to conducting the series of measurements, the ICP-MS was properly optimized both in the standard operation mode and in the DRC-e mode, using appropriate Perkin-Elmer optimizing solutions. Basic optimization criteria included achieving maximum sensitivity to respective chemical elements, the slightest possible signals for oxides (e.g., CeO<sup>+</sup>) and doubly charged ions (e.g., Ba<sup>++</sup>) and the lowest possible background values.

Simultaneously, blank tests were performed using MilliQ (18.2 M $\Omega$ ) water (tests were performed for filtered and unfiltered water). Concentrations of studied metals indicated in the blank tests were taken into account in the final results for respective metals.

Conductivity and total dissolved solids (TDS) were measured with a LF197 conductivity meter (WTW Weilheim, Germany) and pH was measured with a HI 9025 pH meter (Hanna Instruments, Woonsocket, RI, USA). Those parameters were measured immediately in the field while collecting water samples, with an accuracy of up to 0.0 for TDS and conductivity and up to 0.00 for pH.

Subsequently, statistical analysis was applied to the obtained results, conducted with the aid of Statistica 10.1 software (StatSoft Inc. 2011). Pearson's linear regression was calculated for  $\alpha = 0.05$  and principal component analyses (PCA) were conducted. PCA analyses were performed using the mean values for each variable and water body. Standardized values of the chemical parameters were taken into account.

#### **Results**

The pH range and average pH values for water, as well as the conductivity and TDS values, can be found in Table 1. The pH ranged from 6.09 to 8.21, while the average pH value amounted to 7.67. Toward the mouth of the stream, and away from its source, pH tended to increase slightly. The highest difference between water pH values between particular research sites was noted for OC, and at the same time the lowest pH was noted at its source (Fig. 2). Conductivity values ranged from 6.0 to 875  $\mu$ S/cm and TDS values ranged from 7.0 to 975 mg/L, with averages of 170.7  $\mu$ S/cm and 190.7 mg/L, respectively. The lowest values of the aforementioned

**Table 1** Range and average values of the investigated physicochemical indicators in surface waters of the western coast of Admiralty Bay.

				Conductivity	Total dissolved solids
Water body <sup>a</sup>	N <sub>p</sub>	Statistics	рН	μS/cm	mg/L
EG	8	Range	6.88-7.79	6.0-158.7	7.0-177.0
		Mean	7.48	72.40	80.5
WV	8	Range	7.30-8.02	38.7-232	43.0-258.0
		Mean	7.73	122.5	136.5
CC	8	Range	7.10-7.99	132.0-209.0	159.0-233.0
		Mean	7.87	160.1	180.3
VC	8	Range	7.70-7.93	118.8–289.0	133.0-322.0
		Mean	7.83	172.6	192.6
PFC	8	Range	7.80-8.02	156.1-202.0	174.0-227.0
		Mean	7.90	179.5	200.1
OC	12	Range	6.09-7.94	31.3-226.0	35.0-254.0
		Mean	7.28	167.6	187.5
DWR	4	Range	7.66-7.96	143.7-178.8	160.0-201
		Mean	7.81	165.6	184.8
LW	4	Range	7.66-8.21	399.0-875.0	446.0-975.0
		Mean	7.90	580.0	647.0
		Mean	7.67	170.7	190.7

<sup>&</sup>lt;sup>a</sup>Sampled waters are abbreviated as follows: a stream flowing along the border of Ecology Glacier (EG); a stream flowing across the Wróbel Valley (WV); Czech Creek (CC); Vanishing Creek (VC); Petrified Forest Creek (PFC); Ornithologists Creek (OC); drinking water reservoir (DWR); Lake Wujka (LW).

indicators were observed in water samples collected from EG: they were half the average values for the remaining streams. The highest conductivity and TDS values were recorded in the waters of LW, exceeding the corresponding values in the other freshwater reservoirs of Thomas Point Oasis by about three times. Increasing conductivity and TDS values were also noted while

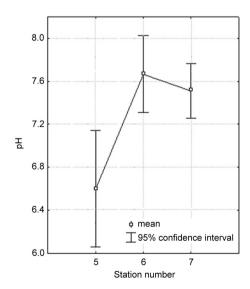


Fig. 2 Variability of pH at sampling stations at Ornithologists Creek: stream mouth (5); middle part of the stream (6); and stream source (7).

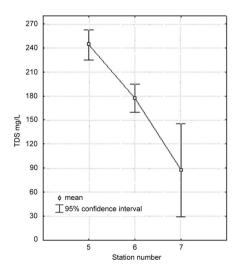
bTotal: 60.

moving away from the source towards the stream mouth, similar to OC (Fig. 3).

Supplementary Tables S1 and S2 provide concentration range, mean values, absolute standard deviation for the entire population and variation coefficient for total concentrations and dissolved fractions of the studied elements.

Concentrations of total elements ranged widely between  $<0.01~\mu g/L$  in the case of Cd and 510  $\mu g/L$  in the case of Fe; both concentrations were recorded in water samples collected from the stream running along EG (Supplementary Table S1).

With regard to mean values, total elements could be divided into three groups. The first group included elements with the highest concentrations, such as Al and Fe, with average concentrations of 17.4 and 67.1 µg/L, respectively. Those elements showed a high level of interdependence, and the calculated correlation coefficients were statistically significant: r = 0.93 (Table 2, Fig. 4). The PCA analysis also indicated the existence of a strong mutual dependence between the two elements (Fig. 5). The second group included Cu, Zn, Pb and Mn, with average concentrations amounting to 1.19, 10.59, 5.55 and 9.08 µg/L, respectively. Within this group, significant correlations were observed between Cu and Zn, Cu and Pb, Cu and Mn, as well as between Zn and Mn. The values of Pearson's correlation coefficient amounted to 0.67, 0.27, 0.64 and 0.30, respectively (Table 2). Finally, the third group included elements characterized by the lowest concentrations: Co, Ni, Cd, As and Se, with average concentrations of 0.16, 0.56, 0.48, 0.57 and 0.08 µg/L,



**Fig. 3** Variability of total dissolved solids (TDS) at sampling stations at Ornithologists Creek: stream mouth (5); middle part of the stream (6); and stream source (7).

respectively. No statistically significant correlations were discovered between elements in this group (Table 2). However, significant correlations were discovered between Co and such metals as Mn and Fe (r=0.69 and 0.31, respectively); a correlation was also discovered between Pb and Ni (r=0.86) (Table 2).

Among studied elements, in the case of Co, Cu and Mn, significant inversely proportional correlations with water pH were discovered, whereas for the remaining metals such correlations were not statistically significant and the directions of correlations varied. With regard to conductivity and TDS, statistically significant correlations were noted for Mn and Se (Table 2). In the case of most studied metals, higher concentrations were discovered in water samples collected from stream mouths in comparison to those collected from stream sources (Table 3). Statistical analysis of the dependence between chemical element concentrations and the distances of the studied streams revealed mostly positive correlations. Statistically significant correlations were identified only for Mn and Se (r = 0.29 and 0.38, respectively). For Cd and As, the dependence on distance was inversely proportional (Table 2).

PCA analysis was applied in order to find dependencies between the studied chemical elements and water bodies, which allowed for reducing 11 variables to three principal components while retaining over 98% of the total variance. The PCA analysis led us to distinguishing two groups of water reservoirs. The first group included OC and LW: water samples collected from those water bodies showed similar concentration levels of Ni, Cu, Zn, Cd, Pb, Mn, Fe and As. The second group comprised the remaining studied reservoirs (Fig. 6). In this group, large disparities were observed from one reservoir to another with respect to concentrations of elements, so it was impossible to break the group into subgroups.

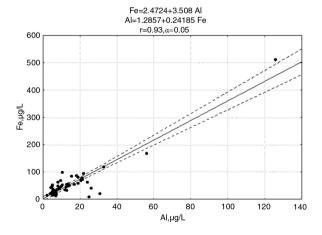
Concentrations of dissolved elements (Supplementary Table S2) may also be described as divisible into three groups. The highest average concentration of the dissolved fraction was recorded in the case of Fe, amounting to 17.5 µg/L. The second group, characterized by average concentrations of dissolved fractions included Al, Zn, Cd, Pb and Mn (5.1, 3.27, 1.95 and 2.35 µg/L, respectively). Finally, the third group, with the lowest concentrations of dissolved fractions included such elements as Co, Ni, Cu, Cd, As and Se (0.05, 0.23, 0.45, 0.08, 0.26 and 0.13 µg/L, respectively). The concentrations of dissolved elements were lower in comparison to total concentrations by the average values of 19% for Se, 29% for As, 49% for Pb, 50% for Cd, 57% for Mn, 59% for Fe, 61% for Co and Ni, 65% for Al and 67% for Cu.

Со Сп Cd Fe Conductivity 0.49\* Co -0.070.06 Ni Сп 0.25 0.58 0.45 0.67 -0.010.25 0.22 7n -0.09 0.10 Cd -011 0.24 0.13 Ph -0.13-0.040.86 0.27\* 0.11 0.07 Mn 0.24 0.69\* 0.14 0.64\* 0.30\* 0.20 -0.04Fe 0.93 0.31\* 0.02 0.22 0.04 -0.07-0.080.13 0.10 As 0.17 -0.04-0.24-0.13-0.07-0.09-0.240.05 0.14 Se -0.14 -0.020.14 0.14 0.11 -0.060.11 0.29\* -0.20-0.70\* -0.02 0.39\* 0.02 0.04 0.09 0.18 рΗ 0.02 0.02 Conductivity -0.18-0.060.03 0.22 0.10 0.08 0.02 0.33\* 0.17 0.15 0.68 0.21 Total dissolved solids -0.060.03 0.22 0.10 0.08 0.02 0.21 1.00\* -0.180.33\* 0.17 -0.150.68 Distance 0.02 0.22 0.26 0.24 0.22 0.08 0.24 0.29\* 0.00 -0.220.39\* 0.11 0.23

**Table 2** Values of Pearson's correlation coefficient (r) regarding total concentrations of the investigated elements, physicochemical indicators and distance in the investigated surface waters. An asterisk indicates statistical significance at P < 0.05.

#### **Discussion**

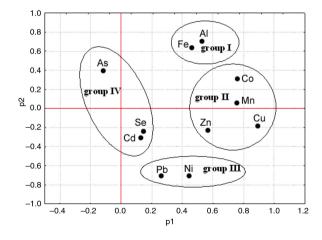
The levels of pH, TDS and conductivity recorded in the course of the study were typical for Antarctic freshwaters. Similar values of these parameters had been given by: Howard-Williams et al. (1989), Sheppard et al. (1997), Vinocur & Unrein (2000), Elster & Komarek (2003) and Toro et al. (2007). The pH of freshwater in Antarctica is affected by such factors as primary production, which increases pH, and the infiltration of ornithogenic soils, which lowers pH. In the study discussed here, an acidic pH level was observed in the water sample collected at the mouth of OC (Fig. 2). Similar results for the same stream were obtained by Elster & Komarek (2003), who posited that they were due to the decomposition of penguin droppings in the catchment area of the stream. The stream flows through ornithogenic soils and, as has



**Fig. 4** The correlation between aluminium and iron in the investigated surface waters of the western coast of Admiralty Bay (statistically significant correlation coefficient).

been pointed out by Juchnowicz-Bierbasz (1999) and Juchnowicz-Bierbasz & Rakusa-Suszczewski (2002), waters infiltrating this type of soils are acidic. The increased pH levels in the remaining reservoirs might be attributable to primary production. Water in Antarctic streams is characterized by low buffer capacity, so pH can increase even with a very low rise in primary production (Toro et al. 2007).

Antarctic streams are supplied by meltwater from glaciers and permafrost, as well as melting snow and rain, and are therefore characterized by low TDS concentrations, which we observed in this study (the lowest TDS and conductivity were recorded in EG). However, due to the effect of sea aerosol, the TDS and conductivity

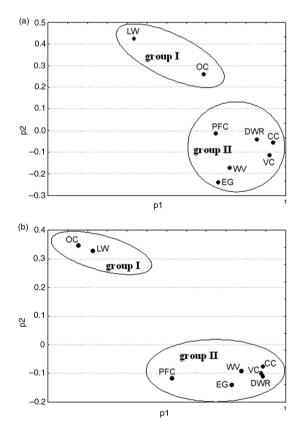


**Fig. 5** The principal component analysis (PCA) results regarding all investigated metals. Taking into account the existing correlations, four groups of metals are distinguished: groups I, II and III included metals displaying very strong correlations within each group; group IV included metals which did not display strong correlations within the group. Total variation for the first two components equaled 49.87%.

Table 3 A comparison of total elements concentrations (average values) at the mouths and sources of the investigated streams.

		Al	Co	Ni	Cu	Zn	Cd	Pb	Mn	Fe	As	Se
Streams <sup>a</sup>	Ν	μg/L										
Mouths												
EG	4	47.2	0.24	0.50	1.57	6.90	0.03	2.29	7.44	192.9	0.24	0.10
WV	4	19.3	0.19	0.29	1.04	7.08	0.03	1.16	7.12	73.0	1.18	0.23
CC	4	5.2	0.05	0.29	0.63	7.37	0.04	1.87	1.36	30.6	0.23	0.12
VC	4	12.7	0.08	0.19	0.65	9.93	0.04	1.35	2.01	44.4	0.18	0.19
PFC	4	7.7	0.05	1.58	1.47	11.49	0.25	15.57	1.89	40.6	0.08	0.19
OC	4	18.3	0.55	0.89	4.20	24.74	0.11	5.33	33.9	33.0	0.11	0.19
Sources												
EG	4	14.0	0.18	0.76	1.49	7.97	0.04	3.73	3.69	59.9	0.13	0.05
WV	4	23.7	0.10	0.20	0.98	6.94	0.05	1.02	5.02	66.9	2.08	0.16
CC	4	6.5	0.04	0.23	0.62	6.41	0.02	1.81	1.12	22.0	0.18	0.10
VC	4	10.0	0.06	0.23	0.60	4.56	0.04	1.09	2.08	40.3	0.20	0.18
PFC	4	6.3	0.06	0.83	1.06	10.22	0.18	10.26	1.45	40.6	0.13	0.13
OC	4	9.3	0.10	0.49	1.24	7.61	0.88	3.39	4.75	36.5	0.22	0.10
Average												
Mouths	24	18.4	0.19	0.63	1.59	11.26	0.08	4.60	8.96	69.1	0.34	0.17
Sources	24	11.6	0.09	0.46	1.00	7.28	0.20	3.55	3.02	44.4	0.49	0.12

<sup>a</sup>Sampled waters are abbreviated as follows: a stream flowing along the border of Ecology Glacier (EG); a stream flowing across the Wróbel Valley (WV); Czech Creek (CC); Vanishing Creek (VC); Petrified Forest Creek (PFC); Ornithologists Creek (OC); drinking water reservoir (DWR); Lake Wujka (LW).



**Fig. 6** Results of principal component analysis of (a) dissolved elements and (b) total elements dividing surface waters into two groups: group I included the OC stream and the LW lake while group II included the remaining streams and the DWR (A - dissolved elements, B - total elements).

may become higher, especially in the littoral zone (Caulkett & Ellis-Evans 1997; Toro et al. 2007). According to Nedzarek & Rakusa-Suszczewski (2007), average rainwater conductivity in the fluvial terrace in the lowest location (2 m a.s.l.) on the western coast of Admiralty Bay equalled 1613 μS/cm. Furthermore, the authors proved that the conductivity of atmospheric precipitation (rain and snow) depended on the power and direction of the wind as well as on the season. They noted higher conductivity in atmospheric precipitation during storms, in the precipitation carried by winds blowing in the north-north-west direction, and in the summer season. In the region of the Admiralty Bay, winds blowing from the north and the north-west prevail during austral summer and are especially powerful in the autumn. Sea aerosol could be responsible for the heightened conductivity and TDS values in LW that were recorded in our study. According to Pociecha (2008), the conductivity of the water in LW was as high as 37°600  $\mu$ S cm<sup>-1</sup>, while water temperature dropped to  $-1^{\circ}$ C.

Total and dissolved concentrations of the studied elements showed considerable variability and, together with the variation coefficient, were similar to those recorded by other authors discussing heavy metal contents in water bodies of Antarctica (e.g., Sheppard et al. 1997; Préndez & Carrasco 2003). For instance, Green et al. (2005) showed that during a 49-h study period there was a 13-fold difference regarding Fe concentrations and in the case of Cd there was a 16.5-fold difference between

the highest and the lowest concentration. Such results indicated that the metals they studied were exceedingly sensitive to the changes of conditions in the stream.

Following the conclusions drawn by Préndez & Carrasco (2003) and Green et al. (2005), it can be assumed that in our study the observed high levels of variation regarding concentrations of selected elements were probably due to the effects of local factors and not due to any influences from beyond the island. The analysed elements could have been washed out from surrounding soils by meltwater from the permafrost and melting glaciers, and could also have originated from local atmospheric dust, including the dust brought down from the atmosphere by rainfall and snowfall as a result of changing directions of the wind (e.g., wind-born dust, sea spray). Some atmospheric dust might even have originated from burned fuels used for heating scientific stations (Loureiro et al. 1992; Ikegawa et al. 1997; Sheppard et al. 1997; Mishra et al. 2004; Lu et al. 2011).

According to Bölter (2011), soils in the studied area are composed of weathered rocks of volcanic origin (mainly basaltic andesites and pyroclastic rocks), as well as a mosaic of sedimentary rocks, similarly to soils in other parts of King George Island. There are also ornithogenic soils, believed to cover ca. 70 ha (Tatur 1989). As shown in Table 4, volcanic rocks and soils of King George Island are characterized by metal concentrations exceeding the average concentrations found in the Earth's crust, with Cu and Mn concentrations being especially high. Therefore, the recorded heightened concentrations of the studied elements may be associated with such natural processes as geochemical weathering of volcanic rocks taking place in catchment areas of the studied water reservoirs, and not necessarily with anthropogenic pollution. This is especially plausible for research sites in places where the Arctowski Station cannot directly affect them.

**Table 4** Metal content in soils and volcanic rocks of Antarctica compared to metal content in Earth's crust (values in mg/kg, except Al and Fe in %).

Matrice	Al	Cu	Fe	Mn	Ni	Pb	Zn
Soil near Ferraz Station <sup>a</sup>	3.44	44	6.15	442	5.1	11.5	52
Soil near Lake Vanda <sup>b</sup>	-	28	1.0	104	11.2	3.9	24
Fildes Peninsula <sup>c</sup>	-	129	5.54	1201	44.0	58	81
Fildes Peninsula <sup>d</sup>	5.86	122	5.7	923	14.3	15.8	58
Volcanic rocks	5.18	111	2.79	1500	12.5	7.7	66
(King George Island) <sup>e</sup>							
Rocks (global average) <sup>f</sup>	4.77	25	4.32	716	56.0	14.8	65

<sup>&</sup>lt;sup>a</sup>Santos et al. (2005)

Comparing the results of our research with data provided by Préndez & Carrasco (2003), we found lower concentrations of most elements. Higher concentrations were discovered only in the case of Pb and Mn, while the concentrations of Co and Al were similar. Préndez & Carrasco (2003) studied surface waters on Fildes Peninsula, in the western part of King George Island, where an airport and scientific stations belonging to Chile, Russia, China and Uruguay were located. The area is subject to much heavier human impact than where our study took place. As pointed out by Campbell et al. (1994), breaking up the surface of soil in Antarctica results in releasing water from the melting permafrost. Precipitating out while the rising groundwater evaporated, mineral salts have accumulated on the surface of Antarctic soils. This phenomenon confirms the existence of a water circulation system transporting dissolved salts. In addition, these salts, which are products of chemical reactions, have a tendency to accumulate in soil until they are washed out by water (Ugolini & Anderson 1973). As shown by Sheppard et al. (1997), areas affected by human activity may be characterized by higher metal concentrations than areas unaffected by such activity. This can be the result of waste storage and releasing solid particles to the atmosphere; such particles can contain, for instance, Pb from fuels and Zn from used car tyres. Anthropogenic activities might be the reason why higher Pb and Zn concentrations were recorded in DRW, LW, PFC and OC, in the immediate proximity of Arctowski Station. Annually, the station burns ca. 100 tonnes of fuel, emitting ca.  $0.2 \text{ kg yr}^{-1} \text{ Pb}$  and  $0.5 \text{ kg yr}^{-1} \text{ Zn}$ (Table 5). Research conducted by Suttie & Wolff (1993) showed very high concentrations of Cu, Cd, Pb and Zn in snow samples collected in the immediate proximity of combustion engines. The further away from the source of exhaust gases, the lower were the metal concentrations, and at the distance of 10 km they dropped to the

**Table 5** Annual fuel consumption and emission of selected metals resulting from fuel burned at the stations located on King George Island (data from Mishra et al. 2004).

	Fuel consumed	Pb	Zn	Cu	Cd	
Station	L/yr	kg/yr				
Arctowski (Poland)	100 000	0.20	0.5	0.1	0.000003	
Artigas (Uruguay)	150 000	0.30	0.75	0.15	0.000005	
Bellingshausen (Russia)	250 000	0.50	1.25	0.25	0.000008	
Ferraz (Brazil)	320 000	0.64	1.6	0.32	0.00001	
Frei (Chile)	1 000 000	2.00	5.0	1.0	0.00003	
Great Wall (China)	250 000	0.50	1.3	0.25	0.000008	
Jubany (Argentina)	240 000	0.48	1.2	0.24	0.000007	
King Sejong (Korea)	273 000	0.55	1.4	0.27	0.000008	
Total	2 583 000	5.20	12.9	2.6	0.000077	

bWebster et al. (2003).

<sup>&</sup>lt;sup>c</sup>Carrasco and Prendez (1991).

<sup>&</sup>lt;sup>d</sup>Lu et al. (2011)

<sup>&</sup>lt;sup>e</sup>Groeneweg & Beunk (1992).

fWedepohl (1995).

background level. In the case of King George Island, exhaust gases should be viewed as resulting from an anthropogenic influence. The island is one of the most heavily populated areas of Antarctica, with eight all-year scientific stations and an airport that belongs to the Chilean station. As the island is easily accessible and its environment is attractive, the area is frequently visited by cruise ships. The resulting exhaust gas emissions may affect a considerable area of the island, and because the distances between particular stations are rather short, negative effects can be overlapping.

The concentration values recorded for most elements analysed by us can be considered close to the geochemical background of the region of Antarctica covered by our study. For instance, high Cu concentrations in the soils of the Antarctic Peninsula and King George Island are connected with copper mineralization and not with anthropogenic pollution (Lu et al. 2011). According to the results of statistical analyses, there are strong correlations between various elements. Especially high correlations have been recorded for Al and Fe, Mn and Cu, Co and Mn, and finally for Co and Fe (Table 2), which implies their terrigenous origin, as the rocks and soils of King George Island are rich in these metals (Table 4).

The structure of catchment areas played an important role in the process of shaping physicochemical conditions of the studied water reservoirs. This fact was confirmed by PCA analysis (Fig. 6). The division of studied water bodies into two groups can be explained by different types of catchment areas characteristic of reservoirs belonging to these two groups. The catchment areas of OC and LW have ornithogenic soils. Additionally, breeding colonies of Adélie penguins (Pygoscelis adeliae) and brown skuas (Catharacta antarctica) occur nearby. Ornithogenic soils are composed of clays containing secondary aluminous and ferriferous phosphates, and have the capacity to retain elements permanently (Tatur 1989). As for the remaining reservoirs, their catchment areas have mainly mineral soils and are hardly affected by the presence of ornithofauna.

The observed increase of conductivity, TDS and concentrations of selected elements further away from the sources of streams and closer to their mouths is typical for lotic waters, in which dissolved substances tend to accumulate over the years (Wetzel 2001). This is particularly notable for major ions, as was shown, for example, for the Onyx River by Green et al. (2005). In their study, they did not observe homogeneous growth of heavy metal concentrations along the course of the river. Similarly, in our study we did not observe uniform accumulation of any of the studied chemical elements along the course of the stream from the source to the mouth. Moreover,

statistically significant correlations regarding the dependencies between the elements and the distances of the studied streams were discovered only in the case of Mn and Se. Rapid particulate scavenging, recycling from pore waters, and local weathering processes are all likely to contribute to longitudinal variations (Green et al. 2005).

The lower concentrations of dissolved elements that we recorded indicated the presence of a considerable share of the studied elements in the solid phase. Similar dependencies were noted by Green et al. (2005), proving that such dependencies were typical for metals in river waters all over the world. It can be assumed, after Préndez & Carrasco (2003), that the elements were absorbed or complexed on suspended mineral and organic particles. Sand transported by strong winds, mineral material carried by meltwater and organic waste could be the source of the particles. The phenomena of metal complexation and absorption are complicated and depend on many factors, amongst others, on the kind of metal, its concentration, the type of absorbent and its active surface and pH, as well as the kind and concentration of organic and inorganic ligands (Vuceta & Morgan 1978; Upadhyay et al. 2002).

Our ability to define factors that affect the processes of reducing concentrations of dissolved elements is limited by the absence of detailed data regarding the content and composition of mineral matter and organic matter. However, the recorded reductions of the studied elements may be associated, as has been suggested by Sheppard et al. (1997), with the reduced solid particle content in water samples, as fine suspended particles provide the material necessary for adsorption of heavy metals. This has been confirmed by analyses of soil samples collected from lake shores and bottom sediments in Antarctica, which showed that the composition of the samples was similar (Mentasti et al. 1998).

### **Conclusions**

Metal concentrations recorded in the studied surface waters of King George Island seem to justify considering them as a reference point with respect to surface waters of other areas of the Earth.

Concentrations of total and dissolved forms of elements were connected with the composition of soils in their surroundings and with atmospheric deposition, mostly took place locally. The increased levels of Pb and Zn concentrations recorded in the immediate proximity of the research station indicated anthropogenic contamination.

Significant changeability regarding concentrations of the studied elements indicated that diversely composed rocks were undergoing dynamic and irregular processes of chemical weathering and elements were being leached from the soil by water; it also suggested that mechanisms of their distribution were multidirectional. They depended on chemical mechanisms and chemisorption, as well as complexation and/or chelation of mineral particles and organic matter. A more detailed evaluation of these mechanisms requires further studies focusing on inorganic complexing agents and the composition of organic ligands.

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