ELEMENTAL COMPOSITION OF SURFACE WATERS IN THE ANTARCTIC PENINSULA AND INTERACTIONS WITH THE ENVIRONMENT

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Abstract. The fast changes in chemical and biological properties of many coastal and inland waters in the last decades reflect the pressure of man on the environment. The surface waters of the Antarctic Peninsula, located far from industrial or populated areas, could eventually be used as background lines. Surface water samples were taken from five lagoons of King George Island, Antarctic Peninsula, and from the Kitiesh Lake. Sample pH and electrical conductivity were analysed *in situ* and in the laboratory, respectively. The dissolved fractions were analysed in 1997 and 1998. Total concentrations only for 1998 were determined in another fraction adjusted to pH 2. Aluminium, Ca, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Sn, Sb, Ba, Bi, and Pb were quantified in all samples by means of inductively coupled plasma-mass spectrometry (ICP-MS). Total and dissolved elemental concentrations were discussed considering the composition of particulate material suspended in the waters removed by streams or by water runoff, or from atmospheric aerosols. Concentrations of dissolved elements change from one lagoon to another. Total and dissolved elemental concentrations could be related to water movement by windstorms, to chemical mechanisms in water and/or to natural and anthropogenic atmospheric factors.

Key words: Antarctic surface waters, local and long-range atmospheric aerosols, snow–water–soil and rock interaction, total and dissolved elements

1. Introduction

Increasing levels of global environmental pollution requires a better understanding of the chemical composition of the various physical environmental compartments in remote areas. Surface waters of the Antarctic Peninsula, located far from industrial and populated areas, should be in a pristine condition and their chemical composition could eventually be used as background lines, as suggested for Antarctica by Bargagli (2000). However, petroleum-related products (Hayharth and Jones, 1992; Ikegawa *et al.*, 1997; Evangelou, 1998); organo-chloride residues

(Peterle, 1969; Peel, 1975); trace and heavy metals have been detected in different Antarctic environments (Bargagli, 2000): in waters (Abollino *et al.*, 1996, Préndez *et al.*, 1996, 1999a), in snow and ice (Boutron and Wolf, 1989) and in atmospheric aerosols (Préndez and Zolezzi, 1982; Artaxo and Rabello, 1992; Rojas *et al.*, 1992; Préndez and Muñoz, 1997).

Heavy metals in the hydrosphere come from natural and anthropogenic sources. The natural materials that go into the hydrosphere come from water runoff or, in the case of lakes and oceans, from stream and river inputs and also from atmospheric aerosols.

In the hydrosphere, chemical species are distributed in three important phases: dissolved or filterable $(0.45\,\mu m)$, suspended particulate matter and sediments (Fergusson, 1990). Flux of different chemical species from the sediments to the waters and *vice versa* is important to control the chemical composition of lakes and oceans (Sayles, 1979). Metals can be retained both by chemisorptions in the particulate matter present in waters, such as oxides or hydroxides particles of Al, Mn, and Fe or on the edges of layer silicate clay minerals and by complexation in organic colloids (McBride, 2000).

Atmospheric aerosols are an important source of elements. Their chemical composition is important to understand pollutants' transport processes over long distances. The volatile elements As, Se, Sb, and Hg can be transported over long distances in gaseous form or as enriched particles, whereas Zn, Cd, and Pb are only transported as particulate matter (Hayharth and Jones, 1992). On the other hand, Ni, As, Se, Cd, and Pb are pollutants originated from fossil fuel combustion (Mattigod and Page, 1983; Evangelou, 1998).

The impact of atmospheric aerosols is also detected in the Antarctica Peninsula at the tropospheric level (Préndez *et al.*, 1989; Pereira, 1990; Loureiro *et al.*, 1992; Rojas *et al.*, 1992; Pereira and Johnson, 1993; Préndez and Muñoz, 1997) as well as at the global Antarctic stratospheric level (Scientific Assessment of ozone depletion, 1991, 1994, 1998).

At King George Island, Antarctic Peninsula, many lakes and lagoons, which are partially or totally defrosted during the summer, change their form and size every year because of the fusion of glaciers or fresh snow. Some of them are used with a minimal treatment as a source of potable water by the scientific bases located in the island (Préndez *et al.*, 1996). However, these authors reported non-negligible quantities of some heavy metals in some of the surface waters of the island.

The objectives of this work are to study the elemental composition of surface waters of King George Island and to discuss the mechanisms that determine the presence of the elements in the suspended particulate matter and in the dissolved fraction. The discussion considers the contributions of the material flowing from the edges of the lagoons and of the soil surrounding the waters as well as a possible pollution due to atmospheric transport of elements originated in the island and/or in other continents.

2. Materials and methods

Surface water samples were taken from King George Island, Southern Shetland Islands, Antarctic Peninsula, at five lagoons named AGAB, BASU, INACH, HSTR and CHNS and at the Kitiesh Lake (KTSH). Map of location and sampling sites are shown in Figure 1. The samples were taken during the 1998 Chilean scientific expedition. In each site, the samplings were done in three points of the longest axis, one at both ends and another one in the centre. The pH was determined *in situ* by means of pH-paper with a precision of 0.1 pH units. The samples were stored in plastic bottles and transported to the laboratory. Electrical conductivities were determined using a conductivity metre microprocessor pH/ion metre WTW, mod. PMX 3000. Throughout the study, the material was previously decontaminated according to the following procedure: (1) washing with detergent, (2) rinsing with drinking water to eliminate detergent, (3) rinsing with distilled water, (4) two successive 1 h shaking treatments with analytical-grade 2% HNO_3, (5) rinsing with distilled water, (6) four rinsing with pure water MilliQ (18.2 MΩ), and (7) drying in stove to 30–35 °C. The dissolved fractions were analysed in a fraction from each water sample filtered through a 0.45 μm polypropylene membrane. Total concentrations were determined in another fraction adjusted to pH 2 with HNO_3 and dispersed by ultrasound for 1 h before filtering. In all cases, Al, Ca, Cr, Mn,
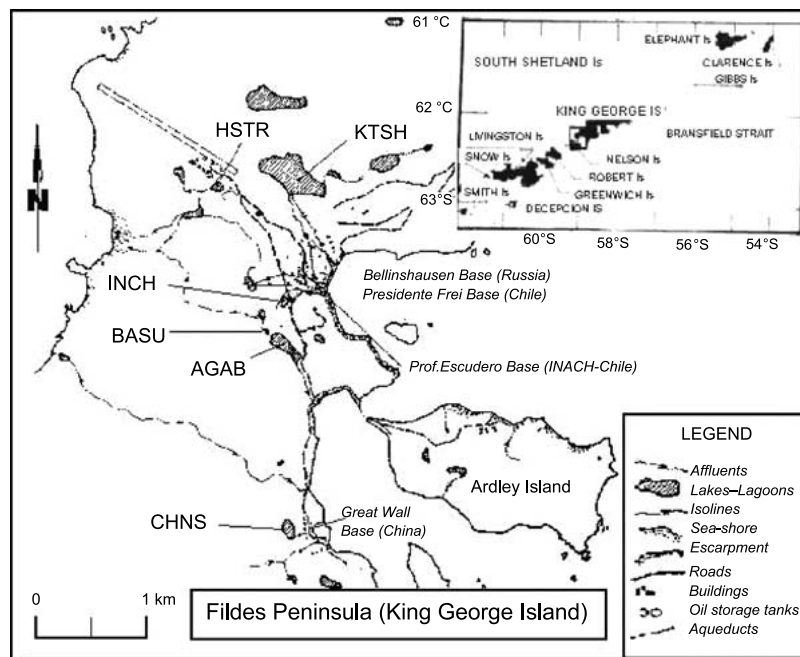

Figure 1. Fildes Peninsula Map, King George Island, South Shetlands Islands, showing lagoons and lake sampled.

Co, Ni, Cu, Zn, As, Se, Sr, Cd, Sn, Sb, Ba, Bi, and Pb were quantified by means of inductively coupled plasma-mass spectrometry (ICP-MS). All the analyses were carried out in duplicate. The multi-standard solutions of SPEX certified standards were prepared with pure water ($18.2\,M\Omega$). The detection limits were calculated as three times the standard deviation. The quantification was carried out at the Study Centre for the Chemistry Development (CEPEDEQ) of the Faculty of Chemical and Pharmaceutical Sciences, University of Chile.

3. Results and discussion

The mean pH in all water samples was 6.0 ± 0.1 units of pH. The electrical conductivity was $237.2 \pm 64.0\,\mu S/cm$ for AGAB, $101.1 \pm 52.8\,\mu S/cm$ for BASU, $84.6 \pm 1.4\,\mu S/cm$ for INCH, $131.9 \pm 5.0\,\mu S/cm$ for HSTR, $117.2 \pm 2.2\,\mu S/cm$ for CHNS, and $143.4 \pm 9.5\,\mu S/cm$ for KTSH.

Tables I and II give concentration ranges, mean values, absolute standard deviations for the total population and variation coefficients for total concentrations and dissolved fractions of the water samples.

3.1. TOTAL ELEMENTS

The total elemental concentrations (Table I) can be grouped into three levels: the first one with the highest concentration corresponds to Ca with 3.0–23.5 mg/L in INCH and AGAB lagoons, respectively; AGAB lagoon has also the highest electrical conductivity ($237.2 \pm 64.0\,\mu S/cm$). The second level, with mean concentrations between 0.2 and $69.8\,\mu g/L$ includes Al, Cr, Ni, Cu, Zn, As, Se, Sr, Ba and Pb; and the third level, with mean concentrations between 0.02 and $1.08\,\mu g/L$, includes Mn, Co, Cd, Sn, Sb and Bi.

The mean total concentrations for Sn and Bi were within the detection limits in all the water samples, while those for Co, Cd and Sb were in the detection limit only for some of them. The mean total concentrations for Ca, As, Sr, Cd, Sb, Bi and Pb (Table I) were below or in the concentration ranges reported by Bowen (1979) for fresh waters (Table III) while the concentration of Se was higher.

For all the elements, total concentrations were below than those reported for 1995 by Préndez et al. (1996) for the same sampling sites.

In coincidence with Bargagli (2000) a comparison of trace metals concentrations from different media in Antarctica with other remote areas of the world is quite difficult. Consequently, he suggests that the Antarctic values should be taken as background values. However, the mean total concentrations for Cu and Zn in all the analysed samples are higher than those given for waters of Terranova Bay (Cremisini et al., 1991). The high Zn concentration at lagoons BASU, INCH and HSTR together with their variation coefficients between 73 and 100% (Table I) would imply a contamination of anthropogenic origin, if the variation coefficient

TABLE I

Concentration ranges, mean concentrations, absolute standard deviations and variation coefficients for total elements in Antarctic superficial waters, year 1998

Pond	N^a	Statistics	Total element concentration (µg/L)							
			Al	Ca	Cr	Mn	Co	Ni	Cu	Zn
AGAB	3	Range	10.8–15.7	23362–23676	<0.2–2.9	<0.05–1.24	0.1–0.5	<0.1–1.5	<0.1–3.9	5.4–17.0
		Mean[b]	13.8	23519	1.1	0.63	0.3	0.9	2.3	11.3
		ASD[c]	2.2	157	1.3	0.49	0.2	0.6	1.6	4.7
		VC (%)[d]	16	1	116	77	68	65	70	42
BASU	3	Range	17.0–30.0	1380–10695	<0.2–1.7	<0.05–1.40	<0.1–0.3	<0.1–23.0	3.2–10.0	16.3–105
		Mean	21.4	6038	0.7	0.72	0.2	7.9	5.8	52.0
		ASD	6.1	4657	0.7	0.55	0.1	10.7	3.0	38.2
		VC (%)	28	77	93	76	57	134	53	73
INCH	3	Range	15.6–24.0	3043–3069	0.4–1.9	0.05–1.10	<0.1–0.9	0.5–5.0	1.7–20.0	16.2–150
		Mean	19.8	3056	1.4	0.58	0.4	2.1	7.9	62.1
		ASD	3.4	13	0.7	0.43	0.4	2.0	8.6	62.2
		VC (%)	17	0	50	74	103	95	109	100
HSTR	3	Range	13.2–17.0	5680–5812	<0.2–2.0	<0.05–0.82	<0.1	<0.1–0.7	2.6–6.0	6.9–61.0
		Mean	14.7	5746	0.8	0.50	0.1	0.3	3.9	27.4
		ASD	1.6	66	0.8	0.33	0.0	0.3	1.5	23.9
		VC (%)	11	1	105	66	0	79	37	87

TABLE I

(*continued*)

Pond	N^a	Statistics	Total element concentration (µg/L)							
			Al	Ca	Cr	Mn	Co	Ni	Cu	Zn
KTSH	3	Range	1.0–14.0	5155–5776	<0.2–2.6	0.05–1.20	<0.1	<0.1–0.3	<0.1–5.8	7.0–18.5
		Mean	8.3	5466	1.0	0.68	0.1	0.2	3.1	12.8
		ASD	5.4	310	1.1	0.48	0.0	0.1	2.3	4.7
		VC (%)	66	6	113	70	0	57	75	37
CHNS	3	Range	5.3–23.0	4633–4899	<0.2–2.3	0.00–1.50	<0.1	0.0–5.0	2.3–9.0	16.0–22.4
		Mean	11.4	4766	0.9	0.52	0.1	1.7	4.8	18.1
		ASD	8.2	133	1.0	0.70	0	2.3	3.0	3.0
		VC (%)	72	3	110	135	0	137	63	17
Detection limit			0.1	7	0.3	0.05	0.1	0.1	0.1	0.2
			As	Se	Sr	Cd	Sn	Sb	Ba	Pb	Bi
AGAB	3	Range	1.09–5.2	4.0–10	69.2–70.3	0.04–0.50	<0.2	<0.2–0.5	0.9–1.1	<0.1–2.9	<0.1
		Mean	3.6	7.4	69.8	0.04	0.2	0.03	1.1	1.9	0.1
		ASD	1.9	2.5	0.5	0.00	0.0	0.01	0.1	1.2	0.0
		VC (%)	52	34	1	10	0	47	12	67	0
BASU	3	Range	<0.1–3.6	<0.1–3.4	6.2–30.6	<0.04–3.15	<0.2	0.03–0.07	0.8–41.0	<0.1–4.5	<0.1
		Mean	2.1	1.9	18.4	1.08	0.2	0.04	14.7	3.0	0.1
		ASD	1.5	1.4	12.2	1.47	0	0.02	18.4	2.0	0.0
		VC (%)	70	72	66	136	0	47	125	68	0

TABLE I
(*continued*)

	a										
INCH	3	Range	<0.1–3.5	1.0–7.0	11.3–11.3	<0.04–0.60	<0.2	<0.2–0.2	0.9–42.0	<0.1–2.7	<0.1
		Mean	2.3	4.7	11.3	0.23	0.2	0.02	14.8	1.7	0.1
		ASD	1.6	2.6	0.0	0.26	0.0	0.00	19.5	1.2	0.0
		VC (%)	68	56	0	116	0	0	132	67	0
HSTR	3	Range	0.2–4.2	3.0–6.0	19.0–19.4	<0.04	<0.2	<0.02–0.03	0.5–14.0	<0.1–1.1	<0.1
		Mean	2.7	4.7	19.2	0.04	0.2	0.03	5.2	0.7	0.1
		ASD	1.8	1.3	0.2	0.00	0.0	0.01	6.5	0.5	0.0
		VC (%)	66	27	1	0	0	21	126	61	0
KTSH	3	Range	<0.1–4.2	2.0–7.2	20.7–22.8	<0.04	<0.2	<0.02	0.9–1.4	<0.1–2.9	<0.1
		Mean	2.7	5.0	21.8	0.04	0.2	0.02	1.2	1.6	0.1
		ASD	1.8	2.2	1.0	0.00	0.0	0.00	0.2	1.2	0.0
		VC (%)	68	44	5	0	0	0	18	71	0
CHNS	3	Range	0.5–3.7	2.0–5.0	19.0–19.9	<0.04–0.05	<0.2–0.7	0.00–0.11	0.9–1.7	<0.1–3.4	<0.1
		Mean	2.4	3.9	19.5	0.04	0.4	0.07	1.2	1.8	0.1
		ASD	1.4	1.4	0.5	0.00	0.2	0.05	0.4	1.4	0.0
		VC (%)	57	35	2	11	64	71	30	74	0.0
Detection limit			0.3	0.1	0.1	0.04	0.2	0.02	0.1	0.1	0.1

[a] Number of observations.
[b] Mean value including observations below detection limits.
[c] ASD = absolute standard deviation for the total population.
[d] VC = variation coefficient.

TABLE II

Concentration ranges, mean concentrations, absolute standard deviations and variation coefficients for dissolved element fraction in Antarctic superficial waters, year 1998

Pond	N^a	Statistics	Dissolved element fraction (µg/L)									
			Al	Ca	Cu	Zn	As	Se	Sr	Sb	Ba	Pb
AGAB	8	Range	<0.4–9.2	22302–23283	0.7–2.7	<0.2–51.0	0.9–4.9	2.0–6.0	66.4–68.1	0.00–0.10	0.7–1.7	<0.1–0.4
		Mean[b]	3.7	22793	1.3	10.7	2.4	4.2	67.3	0.04	1.1	0.2
		ASD[c]	3.2	491	0.7	15.6	1.3	1.3	0.8	0.03	0.3	0.1
		VC (%)[d]	84	2	55	145	100	30	1	77	29	62
BASU	10	Range	<0.1–30.0	1259–10627	0.5–2.0	<0.2–31.0	0.6–3.4	1.9–4.1	5.5–29.1	<0.02–0.1	<0.3–1.7	<0.1–0.2
		Mean	5.5	7458	1.1	10.2	1.5	2.8	20.8	0.04	0.8	0.1
		ASD	8.8	4384	0.5	11.3	1.0	0.9	10.8	0.03	0.4	0.0
		VC (%)	158	59	46	111	66	33	52	73	48	27
INCH	5	Range	<0.1–4.4	2863–2941	0.1–0.8	0.2–8.7	0.7–2.9	3.0–5.0	10.3–10.4	<0.02–0.05	0.2–1.6	<0.1 to <0.1
		Mean	1.9	2902	0.5	3.5	1.9	4.0	10.4	0.03	0.8	0.1
		ASD	2.1	39	0.3	3.1	0.9	0.9	0.05	0.01	0.5	0.0
		VC (%)	111	1	58	91	45	22	0	52	69	0

TABLE II

(*continued*)

HSTR	6	Range	<0.1–4.4	5530–6600	0.7–1.6	0.46–7.60	0.8–4.1	3.0–4.1	18.6–19.6	<0.02–0.04	0.43–1.15	<0.1 to <0.1
		Mean	2.0	5768	1.1	2.8	1.9	3.5	19.1	0.03	1.0	0.1
		ASD	1.9	336	0.4	2.5	1.4	0.5	0.7	0.01	0.6	0.0
		VC (%)	95	6	35	90	74	16	4	31	57	0
KTSH	6	Range	<0.1–4.4	5294–6071	0.4–1.1	0.7–9.2	1.1–3.2	3.5–6.0	18.6–22.5	<0.02–0.03	<0.40–2.26	<0.1–0.2
		Mean	1.8	5682	0.7	3.3	1.9	4.6	20.6	0.02	1.5	0.1
		ASD	2.1	550	0.3	3.0	0.8	1.1	2.8	0.01	0.6	0.1
		VC (%)	116	10	41	91	41	25	13	22	45	39
CHNS	7	Range	0.3–4.4	4478–5079	0–1.6	<0.2–7.9	1.2–4.0	2.5–6.0	19–20	0–0.1	0–1.5	<0.1–0.4
		Mean	1.7	4738	0.7	4.2	2.6	4.2	19.7	0.06	0.9	0.1
		ASD	1.9	309	0.5	2.6	1.4	1.2	0.6	0.04	0.5	0.1
		VC (%)	114	7	72	63	55	29	3	59	57	79
Detection limit			4.4	30	0.6	1.9	0	4.1	0.2	0.03	0.2	0.1

[a] Number of observations.
[b] Mean value including observations below detection limits.
[c] ASD = absolute standard deviation for the total population.
[d] VC = variation coefficient.

TABLE III

Levels of concentration of some elements in fresh and superficial waters

Element	Fresh waters		Superficial waters	
	Concentration (μg/L)	Range (μg/L)	Terra Nova Bay, range (μg/L)[a]	King George Island, range (μg/L)[b]
Al	NI[c]	NI	NI	82–276
Ca	15.0[d]	NI	NI	9303–26713
Cr	NI	NI	NI	41–285
Mn	NI	NI	NI	NI
Co	NI	NI	0.003–10	28–30
Ni	NI	NI	0.03–2.9	30–244
Cu	NI	NI	0.013–1.7	111–273
Zn	NI	NI	0.14–9.0	27–236
As	0.5[e]	0.2–230[e]	NI	1.1–145
Se	0.2[e]	0.002–1[e]	NI	2.3–105
Sr	0.07[d]	NI	NI	NI
Cd	NI	0.01–3[e]	5×10^{-4}–0.04	36–233
Sn	NI	NI	NI	52–56
Sb	0.2[e]	0.01–5[e]	NI	73–447
Ba	NI	NI	NI	588–352
Pb	3[e]	0.06–120[e]	NI	NI
Bi	0.02?[e]	NI	NI	BLD–152

[a] Cremisini *et al.* (1991).
[b] Préndez *et al.* (1996).
[c] NI: no information.
[d] Fergusson (1990).
[e] Bowen (1979).

criterion proposed for soils by Carrasco and Préndez (1984) is used. Different authors (Vera, 1992; Muñoz, 1996; Alcota, 2000) have reported the presence of punctual and irregular quantities of Zn in the atmospheric aerosols emitted by incineration and large quantities in precipitation (Préndez *et al.*, 2001) at King George Island. Both observations would explain the higher concentration of Zn in waters.

3.2. DISSOLVED ELEMENTS

The elemental concentrations in the dissolved fraction, dissolved elements, given in Table II can be grouped in two levels: the first one, with mg/L concentrations, included only Ca whose mean concentration varied from 2.9 (INCH) to 22.8 mg/L (AGAB) depending on the lagoon. The second level included the μg/L concentrations with different sub levels; the concentration of Sr varied from 10.4 to 67.3 μg/L; the concentrations of Al, Zn, As and Se varied from 1.5 to 10.7 μg/L; those of Cr, Mn, Cu, Sn and Ba varied from 0.2 to 1.5 μg/L, and those of Sb and Pb varied from 0.02 to 0.2 μg/L. Chromium, Mn, Co, Ni, Cd, Sn and Bi were always below or in the detection limit, whereas the concentrations of Al, Sb, and Pb were below the detection limit in one or more of the waters under study.

The concentrations of the dissolved elements are in the same order of magnitude than those informed for year 1997 by Préndez *et al.* (1999a, b) for the same waters. In 1998, the concentrations were lower for Al, Cr, Ni, Cu, Cd and Sb and higher for Zn, Se and Ba, than the concentrations obtained in 1997.

The dissolved concentrations of Al, Cu, Zn and Pb are lower than total concentrations (72% or more) except for Cu and Zn, whose dissolved concentrations decrease in lagoon AGAB in 43 and 5%, respectively. The dissolved concentration of Ba showed an important decrease in relation to total concentration in three lagoons: BASU and INCH (95%), and HSTR (81%). The dissolved concentration of As and Se decreased between 7 and 48% in relation to their respective total concentrations.

3.3. GENERAL DISCUSSION

The wide variation in the contents of total and dissolved elements (Tables I and II) as in the variation coefficients might be attributed to local contributions rather than to a general contribution of elements over the island. The local contribution could be due to the surrounding soil flowing to the lagoons, to defrosted water, and to local atmospheric aerosols, including the washing of the atmosphere by rainfall influenced by the changing directions of the winds. Some atmospheric aerosols of anthropogenic origin may come from combustion as a result of use of petroleum for house heating (Hayharth and Jones, 1992; Loureiro *et al.*, 1992; Vera, 1992; Ikegawa *et al.*, 1997).

Total and dissolved concentrations of Ca and Sr are always similar and they probably form soluble compounds, mostly chlorides and a few nitrates. Dissolved

Ca and Sr concentrations correlate with electrical conductivity with $r = 0.932$ ($p < 0.01$) and $r = 0.9564$ ($p < 0.01$), respectively. Total Ca and Sr concentrations correlate with electrical conductivity with $r = 0.965$ ($p < 0.01$) and $r = 0.9655$ ($p < 0.01$), respectively.

The decreasing in some element concentration when dissolved and total element concentrations are compared indicates that most of the elements tend to be adsorbed in the particulate matter. The presence of mineral and colloidal particles as well as the pH are factors that affect the concentration of dissolved heavy metals in the water.

The high concentrations of Ca in waters could be partly explained by the deposit of marine atmospheric aerosols (Contreras *et al.*, 1991; Loureiro *et al.*, 1992; Ikegawa *et al.*, 1997; Préndez and Muñoz, 1997) and partly by the chemical weathering of rocks and soil that are not covered by snow during summer (Smith, 1985; Förstner, 1986; Torri *et al.*, 1989).

The higher total and dissolved concentrations of Ca and Sr were obtained in the lagoon AGAB. Calcium may come from the built-in particulate matter to waters from the borders or from soil runoff, since some soils of Antarctic Peninsula have a low level of leaching and consequently a high base saturation (Luzio *et al.*, 1987), and they are even described as saline soils (Hall *et al.*, 1993).

The concentrations of Ca and Sr, even though high when compared to the other elements, are within the ranges reported for fresh waters by Bowen (1979) and surface waters (Cremisini *et al.*, 1991; Préndez *et al.*, 1996) (Table III). AGAB is also the lagoon with the highest electrical conductivity.

The composition of ionic species in inland and coastal waters is similar to that of local snow and waters derived from the fusion of glaciers (Torri and Yamagata, 1981). However, the distance between the water body under study and the sea, and the high variability of the direction, speed and intensity of winds modify the atmospheric contributions of Na, Mg, Ca and anions like Cl^- and SO_4^{2-} (Muñoz, 1996). Winds may also be responsible for the variable contributions of the different elements present in limnic sediments (Contreras *et al.*, 1991). This information would allow postulating that the differences detected in the waters under study would be reflecting possible local additions as a result of the discharges produced by the own activities of the Antarctic bases. The atmospheric contributions generated in populated areas on remote zones are relatively homogenous; however, a general aerial contribution on the island cannot be completely discarded at least for certain elements, since it has been described as an extra continental contribution of atmospheric aerosols (Murozumi *et al.*, 1969; Boutron and Wolf, 1989; Préndez *et al.*, 1989; Pereira and Johnson, 1993; Alcota, 2000; Bargagli, 2000).

The atmospheric deposit can also be an important source of heavy metal on the zones that remain frozen most of the year and by the way the snow falls on the lagoons. The particulate matter is emitted to the atmosphere by anthropogenic combustion activities and its transport depends on factors like meteorological conditions and size, forms and chemical properties of the aerosol. The quantified Zn,

As and Se could come from the combustion of the petroleum used for heating the Antarctic bases (Hayharth and Jones, 1992; Loureiro et $al.$, 1992; Vera, 1992; Evangelou, 1998). In addition, As and Se could also come from seawater spray; the mean elemental concentration range in ocean waters for As is 0.5–3.7 μg/L and for Se is 0.05–0.2 μg/L (Fergusson, 1990). However, the mean elemental concentration range in the superficial waters quantified in this work is 2.1–3.6 μg/L for total As and 18.4–69.9 μg/L for Se. Thus, only As could come from seawater spray.

Total Cd concentrations, the highest in lagoons BASU and INCH, are in the concentration range given by Bowen (1979) for fresh waters, but are much lower than those reported for 1995 by Préndez et $al.$ (1996) (see Table III). This difference could be explained by a very specific local contamination in 1995 or some irregular process that happened in sediments or adjacent soils. It must be emphasized that pure water is very reactive and that concentrations of Cd in soils of the island reported by Carrasco and Préndez (1991) and Aponte (1998) are higher than the values given for the terrestrial crust by Mason (1966). Windstorms may increase the suspended fine materials in the lagoons; Contreras et $al.$ (1991) have reported variability in electrical conductivity, pH and redox potential produced by the influence of wind in the Kitiesh Lake (KTSH). Another explanation for the very different concentrations of total Cd found at the beginning of January in 1995 (Préndez et $al.$, 1996) and at the beginning of February in 1998 (this work) is related to the phytoplankton bloom. The relatively high cadmium concentration in some waters at the beginning of summer may decrease in about one order of magnitude because of absorption by the phytoplankton bloom (Bargagli, 2000).

The increased total concentrations of Al in the BASU and INCH lagoons could be due to the contribution of stream inputs containing soil colloidal particles in suspension or to the particulate materials released either by the soil surrounding the lagoons or by water runoff. The fine material removed from the borders may remain in suspension due to the low saline content of the waters whose electrical conductivities are between 85 and 132 μS/cm. Soils normally present serious problems of dispersion when its electrical conductivity is smaller than 200 μS/cm (Ayers and Westcot, 1987). In addition, this suspended fine material would provide the necessary material for the adsorption of heavy metals, hypothesis that is reinforced with the results of Mentasti et $al.$ (1998), who demonstrated that the soil samples taken from the border and the sediments taken from the bottom of the lakes in Antarctica have similar composition.

The decrease in the concentrations of some dissolved metals with respect to their total concentrations would indicate that the metals are adsorbed or complexed on the suspended particulate matter. Hering and Morel (1990) indicate that the extension of the organic complexation varies from close to 100% for Cu(II) in coastal waters to a negligible complexation for Mn(II) and Cd; therefore, Cd would be chemisorbed on the inorganic suspended particulate matter in the water, which could come from the soil bordering the lagoons. We postulate that the chemisorption mechanism occurring on the surface of oxides and hydroxides of Al, Mn, and

Fe and even on the edges of layer silicate clays (McBride, 2000) would also occur in the suspended particulate matter in the waters.

The soluble Cd in the waters analysed in this work was below the detection limit, therefore, the formation of some complexes such as $CdCl^+$, $CdCl_2$ or $CdCl_3^-$ could be ignored.

Aluminium is practically insoluble between pH 5 and 7.5 (McLean, 1976); on the other hand, at the pH found in Antarctic waters (pH 6), Al forms $Al(OH)_2^+$, which would adsorb on the colloidal particles in the waters, and $Al(OH)_3$ would precipitate in smaller proportion (Marion *et al.*, 1976). Bismuth and Pb in the waters would precipitate as hydroxides considering that $Bi(OH)_3$ precipitates at pH 4.1 and $Pb(OH)_2$ at pH 5.1 (Fergusson, 1990), explaining their respective dissolved concentration decrease in a range 89–100%.

4. Conclusions

Except for Ca and Sr, the elemental concentrations were at ultra trace levels, challenging analytical detection limits. The low total concentrations of Co, Sn, Sb, and Bi (0.02–0.2 µg/L) in surface waters of the King George Island permits us to consider them background values or baselines for surface fresh water.

The concentrations of total and dissolved elements are related to the composition of the particulate material contained in the soil surrounding the lagoons, increased by streams, by water runoff or by local or remote atmospheric aerosols. Both concentrations vary every year and according to the lagoon, confirming the significance of anthropogenic emissions and/or local natural factors (e.g. precipitation, winds, temperature changes). The interrelations between the contents of total and dissolved elements would be related to water movement and to the chemical processes occurring in soils or in lagoon sediments together with natural and anthropogenic atmospheric factors.

The concentration o the elements in the dissolved fraction depends on chemical mechanisms namely, chemisorption on the surface of inorganic colloids (Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn); complexation and/or chelating by the organic matter present (Co, Ni, Cu, Zn); precipitation of hydroxides (Al, Bi, Pb); and formation of hydroxilated species (Al). In addition, Cd concentration may also depend on the absorption by phytoplankton bloom.

The atmospheric mechanisms affecting the total and dissolved elements in the Antarctic Peninsula include sources of local origin, for example, Ca, Sr and As from marine aerosols; Zn generated by incineration and transported by winds or rainfall; and some other heavy elements, like Pb after long-range transport.

Total Cd quantification in the soil surrounding the lagoons as well as a study of the lagoon phytoplankton should be done in a further study to reinforce our proposals. In addition, the organic ligand concentration should be determined to evaluate its significance in the composition of the waters of the Antarctic Peninsula.

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