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Waterborne metal levels in four freshwater lakes from Harmony Point, Nelson Island, Antarctica

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Abstract: The aim of this study is to analyze the waterborne metal levels in four lakes (one endorheic and three exorheic) of Harmony Point, Nelson Island, Antarctica. Water samples were analyzed by using a quadrupole type inductively coupled plasma mass spectrometer and an inductively coupled plasma optical emission spectrometer. The levels of As, Cu, Mn, Mo, and V were significantly lower and those of Cr, Mg, Na, and Sr were significantly higher in the endorheic lake than in the other lakes. Most water samples presented levels of Ag, Be, Cd, Pb, Se, Tl, and U below the limit of quantification, while for Ba, Co, and Ni around half of the samples were below this limit. The waterborne metal levels were not significantly different between the exorheic lakes. Waterborne metal levels in the freshwater lakes from Harmony Point did not show any clear relationship with their levels in the soil of the region or with bird guano, and overall, their levels indicate an environment without anthropogenic influence. Apparently, the Na levels are influenced by salt spray from the ocean, as they are related to the distance of the lakes from the ocean.

Key words: hydrochemical, limnology, periglacial environments, salt spray.

INTRODUCTION

Antarctic freshwater lakes are dependent on the melting of glacial ice habitats (Cantonati et al. 2020) and their area is continuously increasing due to climate warming (Rosa et al. 2022). Several studies analyzed the limnology and anthropic impact on water channels and lakes from the Antarctic Peninsula: King George Island (Souza et al. 2012, Nedzarek et al. 2014, Bueno et al. 2018, Chu et al. 2019, Lopes et al. 2021, Sparaventi et al. 2022), Seymour Island (Gargiulo et al. 2021), James Ross Island (Lecomte et al. 2020), Deception Island, Livingston Island (Toro et al. 2007, Centurion et al. 2022) and from the main Antarctic continent: Terra Nova Bay (Conca et al. 2017, Zelano et al. 2017), Enderby Land (Kakareka et al. 2019), Larsemann Hills (Nuruzzama et al. 2021), and Windmill Islands (Koppel et al. 2021). Besides direct human contamination (Yin et al. 2006), penguins, petrels, and gulls can also transport metals and contaminate lacustrine environments with their feces (Chu et al. 2019, Chen et al. 2020, Castro et al. 2022, Lopes et al. 2022), since metal contamination occurs in coastal Antarctic areas (Potapowicz et al. 2020, Finger et al. 2021, Sparaventi et al. 2022).

Nelson Island has 164.8 km^2 and is in the middle of the South Shetland Islands, located in Maritime Antarctic. Most of this island (95%) is covered by a permanent ice cap, and chemical analysis of the surface snow made around 30 years ago indicated detectable human influence (Rin et al. 1995). From 1989 to 2020, Nelson Island registered 8.4% glacier area loss and 190% increase in lake area (Rosa et al. 2022). Harmony Point, located in the southwest of the island, is an ice-free area (Rin et al. 1995) whose lakes start to thaw in October, become completely thawed in February, and freeze again in March (Rosa et al. 2020). The area of the lakes in Harmony Point increased 56-100% from 1988 to 2020 (Rosa et al. 2022). Analysis of the soils of this region demonstrated phosphatization associated with guano accumulation but that there is low anthropic impact (Rodrigues et al. 2019, 2021a,b). Nevertheless, despite being a protected area, several kinds of anthropic debris (charcoal, rubber, plastic, and metal) were found recently (Finger et al. 2021). However, the contamination by metals in the freshwater lakes of this region has not been investigated. Therefore, the aim of this study is to analyze the waterborne metal levels in four lakes of Harmony Point to determine if human contamination has affected the freshwater of a protected Antarctic environment.

MATERIALS AND METHODS

Study area

Harmony Point is an area of Nelson Island whose lakes remain thawed in summer (Rosa et al. 2020), and they contain very low levels of chlorophyll, electrical conductivity, and turbidity (Rosa et al. 2021). This area consists of the tip of the island which is surrounded by the Bransfield Strait to the southeast and Drake Passage. To the northeast, there is a place where there is predominantly the island's ice cap. The predominant rocks in Harmony Point are altered volcanic rocks, andesitic and dacite lavas, basalts of grayish to greenish dark colors interbedded with volcanic breccias, agglomerates, conglomerates, and tuffs, of Mesozoic to Cenozoic age (Smellie et al. 1984, Machado 1997, Rodrigues et al. 2019). The drier areas are covered by carpets of the mosses *Sanionia uncinate* and *Polytrichastrum alpinum* and wetter regions contain *Sanionia georgicouncinata* and *Warnsdorfia* spp. Other mosses present are *Andreaea gainii* and *Andreaea depressinervis*. Several species of lichens are common in this area: *Acarospora macrocyclus*, *Caloplaca* spp, *Himantormia lugubris*, *Ochrolechia frigida*, *Psoroma hypnorum* and *Cladonia* spp. (Rodrigues et al. 2019). This site is an Antarctic Specially Protected Area (ASPA 133) because it is the breeding ground for several seabird species in the region, among them the southern giant petrel (*Macronectes giganteus*) (Krüger 2019), the Antarctic shag (*Leucocarbo bransfieldensis*) (Oosthuizen et al. 2020), and penguins (*Pygoscelis* sp) (Rodrigues et al. 2021b).

Places of collection

The water samples were collected in 50 mL Falcon tubes in February 2019, from four Antarctic lakes in an ice-free area, located at Harmony Point (Figure 1). The samples were transported by ship at ambient temperature to Brazil. The transportation took two months. According to the landscape description of this area by Rodrigues et al. (2021a), all four lakes are in the upper platform, and therefore, within the same geomorphological context. The spatial distribution of the sampling stations was performed in accordance with the spatial characteristics and accessibility of each lake. These samples were taken at a depth of 15 cm.

Lake 1 is endorheic (Figure 2a). The ocean is located at 530 m to the northwest, 1500 m to the east, and 800 m to the southeast of the lake. Perimeter samples were collected at 2 m from the edge and consisted of 12 equidistant samples taken approximately 52 m from each other. The sampling of the central area of the lake was performed using a boat, and it consisted of three samples. The remaining three lakes are exorheics and interconnected. They were labeled as lakes 2, 3, and 4 (Figures 2b,

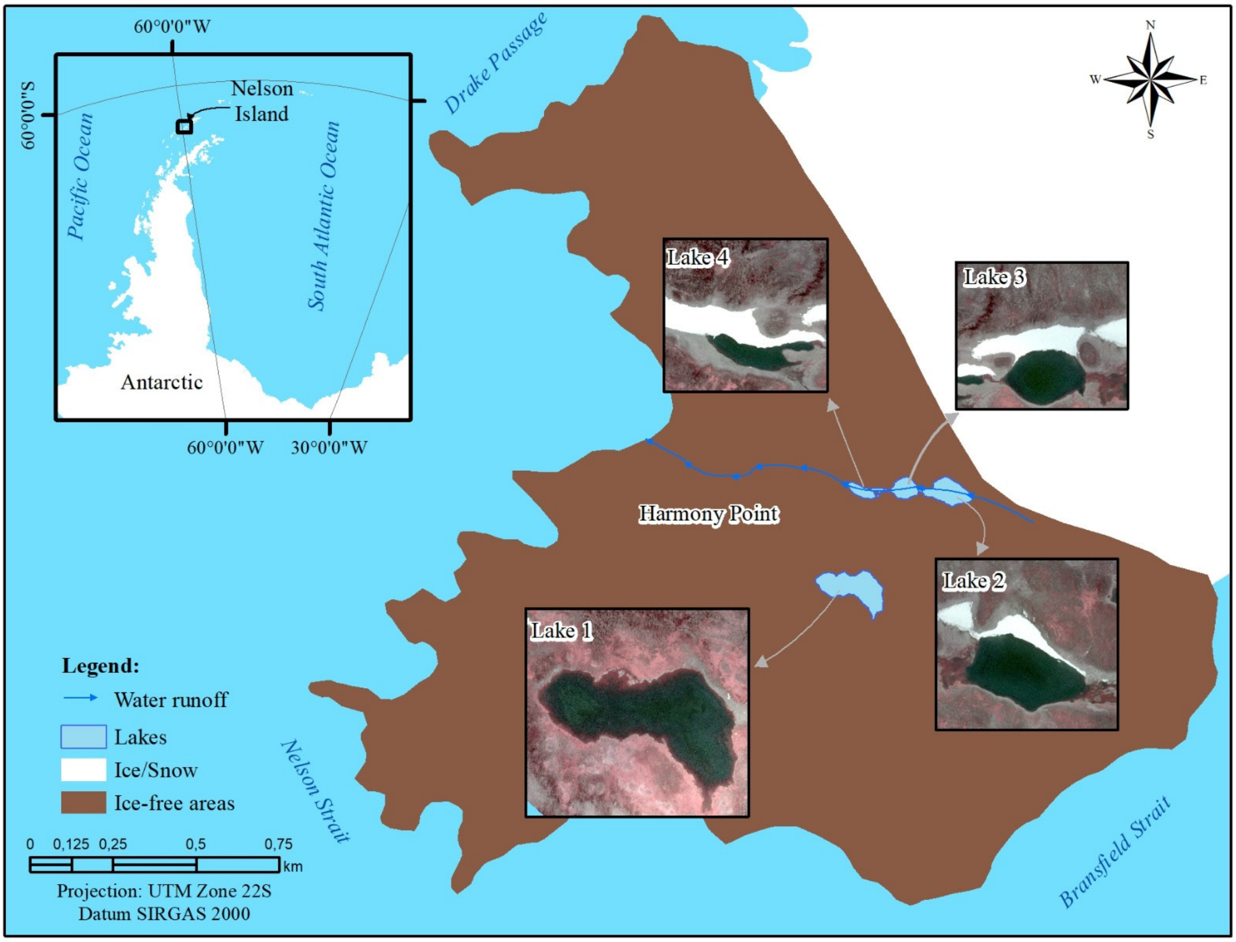

Figure 1. The lakes sampled at Harmony Point, Nelson Island, Antarctic Peninsula.

c, and d) according to the water flow, which is headed west. Therefore, Lake 2 corresponds to a high course at 830 m from the coastline, the third lake represents the medium course at 690 m from the coastline, and the fourth is a low course at 540 m from the coastline. These lakes were sampled only at their outskirts, and two samples were collected on each lake at distances of approximately 60 m from each other (Table I). Lake 1 is inserted in landform patterned ground and the others in cryoplanated platform, following the classification in the platform map of Rodrigues et al. (2019). Based on the same authors, the area of the lakes has permafrost affected soils at a depth between 30 - 38 cm, parent material volcanic tuff and is somewhat poorly drained. The vegetation is mainly composed of rocky mosses *Andreaea* spp and *Sanionia uncinata*.

Instrumentation

Water samples were analyzed at Universidade Federal de Santa Maria (Brazil) by using a quadrupole type inductively coupled plasma mass spectrometer (Perkin Elmer Sciex, Model ELAN DCR II, Canada) and an inductively coupled plasma optical emission spectrometer (model SpectroCiros, CCD, Spectro Analytical Instruments, Germany). The inductively coupled plasma mass spectrometer is equipped with a quartz torch (quartz injector tube of 2 mm i.d.) and a concentric nebulizer fitted to a colonic baffled spray chamber. The inductively coupled

Figure 2. General view of lakes 1 (a), 2(b), 3(c), and 4(d) at Harmony Point, Nelson Island, Antarctic Peninsula. 3c also shows the collection of samples.

plasma optical emission spectrometer is equipped with a cross-flow nebulizer coupled to a Scott double-pass type spray chamber. Argon (99.998% purity) was used for plasma generation. The operational parameters of the ICP-MS and ICP OES instruments are shown in Supplementary Material - Table SI.

Sample analyses

All samples were collected in precleaned 50 mL polypropylene flasks (Sarstedt, Germany) and stored at -20 °C. Before analysis, the samples were thawed to ambient temperature. Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, Tl, U, and V were determined by inductively coupled plasma mass spectrometry (ICP-MS) and Ca, K, Mg and Na by inductively coupled plasma optical emission spectrometry (ICP OES). All analysis was done without any previous treatment or dilution. SRM 1640a was analyzed by ICP-MS and ICP OES in the same form as the samples. The accuracy of the results obtained by ICP-MS and ICP OES for the SRM 1640a water sample was checked at the 95% confidence level (using the t-test).

Reagents and solutions

Ultrapure water (resistivity of 18 MΩ cm) was obtained by a Milli-Q system (Millipore Corp., USA) and was used for material cleaning and solution preparation. Concentrated HNO_3 (65% m m^{-1}, Merck, Germany) was purified in a sub-boiling system (Milestone, Model Duopur, Italy).

Table I. Location of the sampling points in the four Antarctic lakes located at Harmony Point, Nelson Island, Antarctic Peninsula.

Lake	Latitude, longitude	Characteristics
1	62° 18.082'S - 62° 18.145'S 59°12.645'W -59°12.866'W	Endorheic, landform patterned ground, area 13934.2 m^2
2	62° 17.983'S - 62° 17.992'S 59°12.419'W - 59°12.385'W	Exorheic, cryoplanated platform, 5500 m^2
3	62° 17.975'S - 62° 17.974'S 59°12.491'W - 59°12.548'W	Exorheic, cryoplanated platform, 4000 m^2
4	62° 17.962'S - 62° 17.964'S 59°12.593'W - 59°12.670'W	Exorheic, cryoplanated platform, 3500 m^2

Multi-elemental reference solutions containing 10 mg L^{-1} (SCP 33MS, SCP Science, Canada) and 1000 mg L^{-1} (Certipur Merck IV, Merck, USA) were used for calibration in ICP-MS and ICP OES, respectively. The calibration curves and other solutions were prepared in 5% HNO_3 (v v^{-1}). Standard reference material (SRM 1640a, Trace Elements in Natural Water, National Institute of Standards & Technology, USA) was used to check the accuracy of the method.

Statistical analysis

Normality and homoscedasticity of data were checked with Bartlett and Levene tests, respectively. Data from all lakes that fulfilled the requisites (Ba, Ca, Cr, K, Mg, Na, and Sr) were analyzed by one-way Anova and the Tukey test, while non-parametric data (As, Cu, Mn, Mo, Ni, and V) were compared by Kruskal-Wallis and Dunn's test. As lakes 2, 3, and 4 are interconnected and waterborne metal levels were not significantly different between them (see results), the mean of these lakes was also compared with Lake 1 by t-Student or Mann-Whitney tests ($P<0.05$). All data were expressed as mean ± standard deviation (SD).

RESULTS

The results obtained for the trace elements in natural water – SRM 1640a by ICP-MS and ICP OES and the limits of quantification (LOQ) of the methods are in Table II. The LOQ was calculated according to recommendations of the International Union of Pure and Applied Chemistry and considered the blank value and the standard derivation of 10 consecutive measurements of the blank (LOQ = B + 10s, where B is the blank value and s is the standard deviation).

As can be observed, there were no significant differences (*t*-test, 95% confidence level) between certified and determined values obtained from the SRM 1640a. Therefore, both ICP OES and ICP-MS methods are considered accurate for the determination of these elements in the water samples.

Waterborne levels of Ag, Be, Cd, Pb (almost all samples), Se, Tl, and U were below LOQ, while for Ba half of the samples from lake 1, for Co two thirds of the samples from lake 1, all of the lakes 2 and 3, for Cr one lake 1 sample, and for Ni half of the lake 1 samples were below the LOQ. Waterborne levels of Mg were significantly lower in lakes 2 and 3 than in lake 1, and those of Na and Sr were significantly lower in lake 2 than in lake 1. The waterborne levels of As, Mo, and V were significantly higher in lake 4 than lake 1. The waterborne metal levels were not significantly different between lakes 2, 3, and 4. Considering the mean of waterborne levels in lakes 2, 3, and 4, the levels of As, Cu, Mn, Mo, and

Table II. Limit of quantification (LOQ) and results obtained for analysis of the SRM 1640a Trace Elements in Natural Water by ICP-MS and ICP OES. Values are the mean and standard derivation (1SD) for n = 3.

Element	LOQ (μg L^{-1})	SRM 1640a		
		Certified (μg L^{-1})	Determined (μg L^{-1})	Bias (%)
Ag	0.021	8.081 ± 0.046	8.160 ± 0.230	101
As	0.049	8.075 ± 0.070	8.300 ± 0.53	103
Ba	0.027	151.800 ± 0.830	155.37 ± 4.367	102
Be	0.020	3.026 ± 0.028	2.980 ± 0.420	98
Ca	4.150	5.615 ± 0.021*	5.603 ± 0.529*	100
Cd	0.006	3.992 ± 0.074	4.170 ± 0.082	104
Co	0.004	20.240 ± 0.240	20.36 ± 0.70	101
Cr	0.314	40.540 ± 0.300	41.28 ± 0.17	102
Cu	0.067	85.750 ± 0.510	90.13 ± 3.97	105
K	7.160	0.5799 ± 0.0023*	0.5962 ± 0.0044*	103
Mg	0.450	1.0586 ± 0.0041*	1.0380 ± 0.0050*	98
Mn	0.024	40.390 ± 0.360	42.41 ± 1.81	105
Mo	0.009	45.600 ± 0.610	47.22 ± 0.27	104
Na	2.300	3.137 ± 0.031*	3.202 ± 0.046*	102
Ni	0.052	25.32 ± 0.140	26.38 ± 0.78	104
Pb	0.013	12.101 ± 0.050	12.470 ± 0.601	103
Se	1.150	20.13 ± 0.170	20.52 ± 3.41	102
Sr	0.078	126.03 ± 0.910	126.46 ± 5.59	100
Tl	0.001	1.619 ± 0.016	1.600 ± 0.067	99
U	0.001	25.35 ± 0.270	24.76 ± 0.52	98
V	0.056	15.05 ± 0.250	15.32 ± 0.66	102

***Values in mg L^{-1}.**

V were significantly higher and those of Cr, Mg, Na, and Sr were significantly lower than in lake 1 (Table III and Figure 3).

DISCUSSION

As expected, waterborne metal levels in the freshwater lakes of Harmony Point were lower (except As) than those detected by Souza et al. (2012) and Nedzarek et al. (2014) in streams and lakes of King George Island, one of the most populated areas of the maritime Antarctic Peninsula, and lakes close to human settlements in Deception Island (South Shetland Islands) (Sparaventi et al. 2022) and Vecherny Oasis, Enderby Land, East Antarctica (Kakareka et al. 2019) (Table IV). Areas with anthropogenic contamination usually present high waterborne Cu, Mo, Ni, Sr, Pb and Zn levels (Nedzarek et al. 2014, Kakareka et al. 2019), which was not registered in the lakes of Harmony Point (only Zn was not quantified in the current study).

Table III. The concentration of elements in four Antarctic lakes located at Harmony Point, Nelson Island, Antarctic Peninsula. Results were obtained from the analysis of water samples by ICP-MS and ICP OES. The values are the mean ± SD when the concentration of more than one sample was above the limit of quantification (each sample was measured in triplicate).

	Lakes				
Element	**1**	**2**	**3**	**4**	**Mean lakes 2, 3, and 4**
Ag (μg L^{-1})	<0.021	<0.021	<0.021	<0.021- 0.024	<0.021- 0.024
As (μg L^{-1})	0.209±0.052	0.566±0.237	0.742±0.147	0.991±0.097#	0.767±0.232*
Ba (μg L^{-1})	<0.027/0.094±0.088	0.092±0.028	0.076±0.016	<0.027 – 0.145	<0.027 – 0.084±0.021
Be (μg L^{-1})	<0.020	<0.020	<0.020	<0.020	<0.020
Ca (mg L^{-1})	1.372±0.418	0.832±0.206	1.159±0.060	1.732±0.097	1.242±0.421
Cd (μg L^{-1})	<0.006	<0.006	<0.006	<0.006	<0.006
Co (μg L^{-1})	<0.004/0.013±0.002	<0.004	<0.004	<0.004 – 0.035	<0.004 – 0.035
Cr (μg L^{-1})	<0.314/0.644±0.163	<0.314 – 0.316	0.368±0.059	0.417±0.105	0.393±0.075*
Cu (μg L^{-1})	0.578±0.077	1.910±0.424	1.980±0.410	2.890±1.117	2.260±0.747*
K (mg L^{-1})	0.554±0.197	0.212±0.040	0.336±0.045	0.632±0.158	0.394±0.207
Mg (mg L^{-1})	1.750±0.536	0.681±0.199#	0.919±0.139#	1.260±0.102	0.954±0.286*
Mn (μg L^{-1})	0.132±0.024	0.374±0.031	0.381±0.077	0.292±0.166	0.349±0.094*
Mo (μg L^{-1})	<0.009/0.045±0.008	0.080±0.037	0.158±0.052	0.213±0.021#	0.151±0.067*
Na (mg L^{-1})	11.285±3.829	4.030±1.131#	7.495±1.322	7.540±2.998	6.355±2.376*
Ni (μg L^{-1})	<0.052/0.084±0.013	0.108±0.025	0.094±0.047	0.279±0.283	0.161±0.159
Pb (μg L^{-1})	<0.013	<0.013	<0.013	<0.013-0.061	<0.013-0.061
Se (μg L^{-1})	<1.15	<1.15	<1.15	<1.15	<1.15
Sr (μg L^{-1})	10.457±2.560	4.195±1.534#	6.285±1.421	7.475±0.714	5.985±1.784*
Tl (μg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
U (μg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001
V (μg L^{-1})	0.414±0.099	0.793±0.280	0.997±0.230	1.245±0.078#	1.012±0.261*

Significantly different from Lake 1 (considering only samples above the limit of quantification) by the * t-Student or Mann-Whitney tests (means lakes 2, 3, and 4); # one-way Anova and the Tukey test or by Kruskal-Wallis and Dunn's test (P<0.05).

The levels of metals measured in the lakes of Harmony Point are lower or similar to those observed by Conca et al. (2017) and Zelano et al. (2017) in the lakes of Terra Nova Bay, and by Toro et al. (2007) in lakes from Byers Peninsula (Livingston Island), other Antarctic protected areas, as well as in unpolluted lakes of Vecherny Oasis (Kakareka et al. 2019) (Table IV). The only exception is Cu, because lakes 2, 3 and 4 have higher levels than the lakes from Terra Nova Bay (Conca et al. 2017, Zelano et al. 2017). The waterborne As and Cu levels in lakes 2, 3 and 4 of Harmony Point are also the only levels higher than those from the coastal lakes of Larsemann Hills, East Antarctica (Nuruzzama et al. 2021).

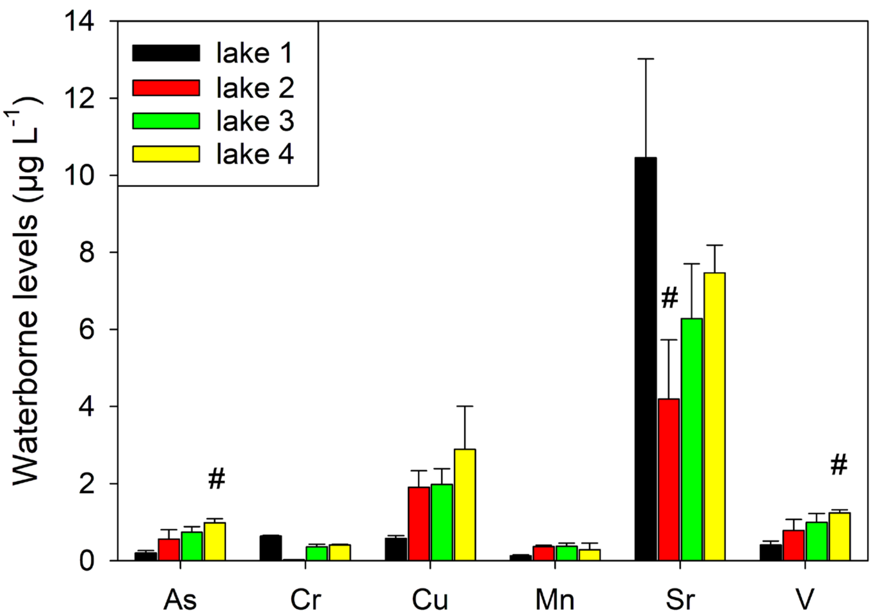

Figure 3. **The concentration of the main elements in four Antarctic lakes located at Harmony Point, Nelson Island, Antarctic Peninsula. The values are the mean ± SD.**
 # Significantly different from Lake 1 (considering only samples above the limit of quantification) by one-way Anova and the Tukey test or by Kruskal-Wallis and Dunn's test (P<0.05).

The differences observed in some waterborne metal levels of lake 1 and lakes 2, 3, and 4 may be associated with the geographic context in which the lakes are located. Lake 1, endorheic, contains lower Cu data than the other lakes, which are exorheic. In this sense, it is noteworthy that lake 1 did not have snow/ice in its catchment area and is a lentic environment, while the other lakes were under snow/ice melting conditions in their hydrographic basin, configuring themselves as a semi-lentic. Therefore, they received water from meltwater and were subject to metal contamination due to leaching from the soils and from the meltwater itself.

Within the determined metal values, Ba, Cu, and V are trace elements with higher concentrations in the soil of the coastal domain from Harmony Point (Rodrigues et al. 2021a) (Table IV), which could explain the presence of Cu and V in the lakes. However, waterborne Ba levels in the lakes were comparatively low, which reduces the possibility of soil origin for these metals. Another possibility to explain the waterborne Cu and Sr levels would be the guano from different seabird species that occur in the region. Nevertheless, the guano of giant petrels, which have several active nests in Harmony Point (Krüger 2019), as well as of gentoo penguins (*Pygoscelis papua*) and kelp gulls (*Larus dominicanus*) contains 2-4-fold higher concentrations of Mn than Cu and Sr (Castro et al. 2022), and waterborne Mn levels are 8-15-fold lower than Cu and Sr levels, but the same authors did not find any relationship between Mn content in the soils and bird guano. Apparently, the levels of As in the soil of Harmony Point, determined by Rodrigues et al. (2021a), also showed a relationship with the waterborne levels, as other metals such as Co and Pb presented higher levels in the soil (Rodrigues et al. 2021a) and waterborne levels close to LOQ. The lower levels of waterborne As in surface waters of King George Island (Nedzarek et al. 2014) than in the lakes of Harmony Point are in disagreement with the hypothesis of anthropic origin of this metal. The waterborne metal levels in the freshwater lakes from Harmony Point, with exception of Cu in lakes 2, 3 and 4, indicated that the waters

Table IV. **The concentration range of elements in four lakes (this study) and soil from horizon A + horizon C of upper platform from Harmony Point (data of Rodrigues et al. 2021), surface snow from the top of Nelson Island (data of Qin et al. 1993), lakes from Byers Peninsula (Livingston Island) (data of Toro et al. 2007), and from Vecherny Oasis, Enderby Land, East Antarctica (data of Kakareka et al. 2019).**

	Lakes Harmony Point	Soils Harmony Point	Snow Nelson Island	Lakes Byers Peninsula	Lakes Vecherny Oasis
Ag (μg L^{-1}/μg kg^{-1})	<0.021- 0.024	-	-	-	nd-0.027
As (μg L^{-1}/μg kg^{-1})	0.209-0.991	3.47-7.16	-	-	0.052-0.990
Ba (μg L^{-1}/μg kg^{-1})	<0.027-0.094	102.98-110.68	-	-	0.753-9.042
Ca (mg L^{-1}/mg kg^{-1})	0.832-1.372	13928-20357	0.036	0.31-16.62	0.14-2.16
Cd (μg L^{-1}/μg kg^{-1})	<0.006	1.03-1.36	-	-	0.001-0.549
Co (μg L^{-1}/μg kg^{-1})	<0.004-0.035	10.38-13.81	-	-	0.005-0.286
Cr (μg L^{-1}/μg kg^{-1})	<0.314-0.644	32.53-41.57	-	-	0.044-12.064
Cu (μg L^{-1}/μg kg^{-1})	0.578-2.260	103.55-134.43	-	-	nd-2.171
K (mg L^{-1}/mg kg^{-1})	0.212-0.554	1244.7-3319.1	0.031	0.17-1.73	0.09-1.17
Mg (mg L^{-1}/mg kg^{-1})	0.681-1.750	2400.0	0.072	0.32-11.95	0.15-1.84
Mn (mg L^{-1}/mg kg^{-1})	0.132-0.374	47.32-55.21	-	-	0.434-31.24
Mo (μg L^{-1}/μg kg^{-1})	<0.009-0.158	1.22-2.00	-	-	0.010-1.603
Na (mg L^{-1}/mg kg^{-1})	4.030-11.285	1854.8-4340.3	0.99	6.57-107.20	1.61-14.93
Ni (μg L^{-1}/μg kg^{-1})	<0.052-0.161	9.28-10.24	-	-	0.046-0.690
Pb (μg L^{-1}/μg kg^{-1})	<0.013-0.061	16.40-27.82	-	-	nd-1.863
U (μg L^{-1}/μg kg^{-1})	<0.001	8.22-8.78	-	-	nd-0.012
V (μg L^{-1}/μg kg^{-1})	0.414-1.245	167.70-192.23	-	-	0.155-3.912

Nd – non detected.

of these lakes are indicative of high ecosystem integrity according to United Nations University (2016) and are below the limits established by the EPA (2022a, b) for aquatic life and human health. The increase of snow melting that has been occurring in the last years in Nelson Island (Rosa et al. 2022) probably contributed to the low waterborne metal levels in the lakes compared to the soil in Harmony Point, as the snow in unpolluted sites has very low metal levels (Qin et al. 1993, Kakareka et al. 2020) (Table IV). Despite the water of these lakes from Harmony Point having low levels of waterborne metals, before any consideration regarding use for human consumption, it is important to determine phosphate (or phosphorus) and nitrate levels as well as bacterial diversity, as these factors are influenced by the occurrence of birds (Mindl et al. 2007, Villaescusa et al. 2013, Zhu et al. 2015), and this region is the breeding ground for several seabird species (Krüger 2019, Oosthuizen et al. 2020, Rodrigues et al. 2021b).

The higher waterborne levels of Na and Mg (but not Ca) in Lake 1 compared to the other lakes may be due to salt spray from the ocean, as Lake 1 is closer to the ocean than lakes 2 and 3. In comparison, the distance of the lakes from the seashore affected more deeply the levels of Na, Ca, Mg, and K in Byers Peninsula, Livingston Island, with the ones closer to the ocean having

16-55-fold higher levels (Toro et al. 2007) (Table IV). The low Mg/Ca ratio determined in the lakes of Harmony Point (0.818-1.275) is also an indication of the low influence of salt spray, because lower values are registered in lakes more distant from the sea (Abollino et al. 2004, Kakareka et al. 2019). Higher Na levels were observed in soils of Harmony Point closer to the ocean, but Mg and Ca levels were similar (Rodrigues et al. 2019, 2022). The levels of Na, Ca, Mg, and K are higher in soils affected by flying birds and penguins in Snow Island (Antarctic Peninsula) (Lopes et al. 2022), but if there was enough leaching from ornithogenic soils to affect the levels of these ions in the lakes, this leaching was similar between lakes, as no significant difference in Ca and K levels were detected.

CONCLUSIONS

In conclusion, waterborne metal levels in the freshwater lakes from Harmony Point present low levels, as observed in lakes of other Antarctic unpolluted sites. There was no clear relationship of waterborne metals with their levels in the soil of the region or with bird guano, and overall, their levels indicate an environment without anthropogenic influence. However, these levels may be associated with the geographic context in which the lakes are located, because lake 1, endorheic, shows some significant differences compared to the exorheic lakes (2, 3, and 4). The Na levels are apparently influenced by salt spray from the ocean, as they are related to the distance of the lakes from the ocean, but the influence of the salt spray in these levels is much lower than observed in other Antarctic lakes. Therefore, these lakes can be used as reference sites for the analysis of environmental perturbations. As Harmony Point is a place with high occurrence of petrels, penguins, and gulls, future studies should investigate waterborne levels of phosphate, nitrate, uric acid, and bacteria.

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SUPPLEMENTARY MATERIAL

Table SI

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