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SEDIMENTS, SEC 1 • SEDIMENT QUALITY AND IMPACT ASSESSMENT • RESEARCH ARTICLE

Trace element distribution and pollution status of surface sediments in lakes impacted by volcanic activity

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Abstract

Purpose The main objective of the study was to assess the environmental quality status of the sediments of eleven Patagonian lakes regarding the concentrations of five trace elements, evaluating the influence of volcanic activity and water and sediment parameters on element concentration and distribution.

Materials and methods Surface sediment samples from 11 lakes were collected at different depths for granulometric analysis, organic matter (OM) contents, and determination of As, Br, Cr, Hg, Ni, and Zn concentrations. Physicochemical variables of the water column were also measured. The quality of the sediments and the potential ecological risks were assessed by comparing the concentrations of elements with local and global geochemical background values and with consensus-based sediment quality guidelines and through the calculation of environmental quality indices (enrichment factor and index of geo-accumulation).

Results and discussion A higher proportion of sand with a lower %OM characterized the surface sediments in lakes close to the volcanic complex (PCCVC), while a higher proportion of silt–clay with a higher %OM was found in sediments from lakes furthest from the PCCVC, consistent with the expected gradient of volcanic ash size deposited in the lakes. The presence of volcanic ashes in sediments seems to dilute trace element concentrations of samples, having sediment samples from lakes near the PCCVC lower concentrations of Br, Cr, and Ni than the furthest lakes. Environmental quality indices indicated minimal to moderate enrichment/contamination in sediments from deep lakes near the PCCVC and significant to high enrichment/contamination in sediments from lakes far from the volcano and in the shallower lakes. The concentrations of As, Cr, and Ni in six of the 11 sampled lakes are at levels considered harmful for sediment-dwelling organisms according to north hemisphere guidelines.

Conclusions Despite being in a protected area, the sediments of some Patagonian lakes have concentrations of potentially toxic elements at levels that may cause pollution and be of risk to the aquatic biota, with the volcanic ashes acting to dilute this effect.

Keywords Potentially toxic elements · Contamination assessment · Lake sediments · Volcanic impact · Patagonia

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1 Introduction

Metals are among the most persistent contaminants in the environment, and because of their toxicity and bioaccumulation, they are a serious concern in terms of their aquatic pollution (Bryan and Langston 1992; Zhang et al. 2014). Since metals, as well as other potentially toxic trace elements, are poorly soluble in water, in aquatic ecosystems, they are mostly bound to suspended particulate matter and ultimately deposited in bottom sediments, concentrations being usually higher in sediments than in water (Calmano et al. 1993; Zhang et al. 2014; Liu et al. 2018; Shyleshchandran et al. 2018). However, in response to chemical and biological factors and certain disturbances, the pollutants accumulated in the sediments can be released into the overlying water, acting as a secondary pollution source and damaging the ecological status of the aquatic system (Fu et al. 2014; Liang et al. 2015; Huang et al. 2020).

The distribution and dynamics of metals and other elements in sediments are controlled by a variety of physical and chemical factors, including sediment grain size, the grain surface-to-volume ratio, organic matter content, surrounding pH, and redox potential variations, in which the relative affinity for organic and fine grain size are main control parameters (Singh et al. 1999; El Bilali et al. 2002; Zhao et al. 2011; Zhang et al. 2014). The finest grains have a greater adsorbing capacity for elements given their larger surface area (Horowitz 1991) and are also the most relevant in the exchange of elements from sediments to benthic organisms (Amiard 1992). Since lake sediments are the main storage reservoir of most pollutants, but also a potential secondary source, they are sensitive and useful indicators for monitoring contaminants in the aquatic environment (Gawel et al. 2014; Wu et al. 2014).

One of the largest problems associated with metal threats to aquatic ecosystems is the potential for bioaccumulation and biomagnification in the food web, causing heavier exposure for some organisms than is present in the environment alone (Chen et al. 2000; Fu et al. 2014). Since bottom sediments also serve as habitats and food sources for benthic organisms, pollutants accumulated in sediments may directly or indirectly threaten the aquatic flora and fauna and ultimately human health and the whole ecosystem (Chen et al. 2000; Suresh et al. 2012; Fu et al. 2014). Therefore, the study of sediments' pollutant contents is an important first approach to assessing the ecological health status of an environment (Roach 2005).

Aquatic ecosystems may receive metals and other potentially toxic elements both from natural and anthropogenic sources. Along with the weathering of rocks and soils in a basin, volcanic activity is considered one of the largest natural sources of many elements to the aquatic environment (Nriagu 1990; Garrett 2000). Whereas these natural processes contribute to the background concentrations, volcanic activity affects specific areas of the planet, and therefore, those areas face particular contributions that imprint particular patterns of element accumulation and distribution (Lamela et al. 2019).

The Andean-Patagonian lakes are distributed throughout the Southern Volcanic Zone (SVZ) of the Andean Range (Stern 2004), an active volcanic region with high historic eruptive frequency and high impact all over Argentinean Patagonia (Naranjo and Stern 2004; Stern 2004; Martin et al. 2009; Collini et al. 2013). Volcanic activity has been pointed out as the main responsible for the higher levels than expected in environments without anthropic impact of arsenic (As), mercury (Hg), chromium (Cr), and zinc (Zn) recorded in sediments and aquatic organisms of certain Andean lakes (Ribeiro Guevara et al. 2005; Arribére et al. 2010; Revenga et al. 2012; Bubach et al. 2015; Daga et al. 2016; Juncos et al. 2016; Montañez et al. 2018). Other elements, such as bromine (Br), were identified as volatile pollutants released during a volcanic eruption (Bubach et al. 2012). Moreover, the importance of surface sediments in the dynamic of trace elements in these aquatic ecosystems was revealed by the close relationship between benthic habitats and element bioaccumulation in benthic organisms (Juncos et al. 2016; Arcagni et al. 2017, 2018). However, although many works have analyzed the lacustrine sediments in the region, most have focused on the composition of volcanic products and their identification in lacustrine sediments for chronological purposes (e.g., Daga et al. 2012, 2014, 2017), but there are no studies that comparatively evaluate whether these lakes with low anthropic impact but frequent volcanic activity are compromised in terms of pollution.

The Puyehue-Cordón Caulle volcanic complex (PCCVC) is the most important volcanic center in the area with three major eruptions in the last 100 years (1921–1922; 1960; and 2011–2012), all with the dispersion of pyroclastic products (ash, gases, and aerosols) (Singer et al. 2008; Daga et al. 2014; Bonadonna et al. 2015). Its latest eruption on June 4, 2011, generated a great amount of ash deposition in the study area. The prevailing westerly winds caused different amounts and sizes of volcanic ash fallout (Masciocchi et al. 2013; Pistolesi et al. 2015). Approximately 15–17 cm of coarse ash fall was deposited in towns 54 km SE of the vent; and 3–4.5 cm of medium to coarse tephra (3–6 mm in diameter) fell in the city of San Carlos de Bariloche, located 100 km SE of the vent (Wilson et al. 2013). This coarser to finer grain size gradient is likely to be reflected in the sediments of the lakes in which the ashes will ultimately be deposited and could be used as a proxy for volcanic impact. Given the great affinity of trace elements for organic matter and finer particles (Singh et al. 1999; El Bilali et al. 2002; Zhao et al. 2011; Zhang et al. 2014), the relative proportions of finest/coarse particles in sediments will influence the element concentrations (Loring and Rantala 1992). This scenario offers the opportunity to assess whether the volcanic activity, through ashes deposited in lake sediments, influences the concentrations of certain elements in sediments and whether ecological effects are likely.

As a first stage of the assessment of the impacts of metals in aquatic systems (Roach 2005), this study aimed to assess the environmental quality status and the potential risks to sediment-dwelling species of the sediments of eleven Patagonian lakes differently impacted by the latest PCCVC eruption regarding the concentrations of As, Br, Cr, Hg, Ni, and Zn. Specifically, the objectives of this research were (i) to determine the concentrations and distribution patterns of the selected elements in surface sediments along 11 Patagonian lakes; (ii) to identify the most important environmental factors affecting the trace element concentrations in surface sediments and the influence of the last volcanic eruption on the sediment element concentrations along the lakes; and (iii) to assess the quality of the sediments and the relative degree of potential risks to sediment-dwelling species posed by the studied elements using geochemical background values, environmental quality indices, and international sediment quality guidelines. To the best of our knowledge, this is the first work assessing the environmental quality of sediments in several southern hemisphere lakes affected by volcanic activity.

2 Materials and methods

2.1 Study area

Eleven lakes were selected for the analysis of sediments, located between 40° 27′S and 41° 40′S in the North Andean Patagonia region (Argentina) (Fig. 1) in the Glacial lakes district of the Southern Andes (Iriondo 1989). The North Andean region is characterized by intense Quaternary glaciation processes affecting the previous structural-tectonic setting. Fluvial and mass movement processes and recent volcanism confer the current features to the study sites. The regional lithology is mainly represented by volcanic deposits, granitic rocks, and volcano-sedimentary complexes, with the metamorphic basement outcropping south to lake Nahuel Huapi (Giacosa et al. 2001; Escosteguy et al. 2013). Almost all lakes under study have a glacial origin, and fluvial courses have clear structural control, draining catchment areas of volcanic, plutonic, and sedimentary rocks in variable proportions, with poor to moderately developed volcanic soils. High mountain streams show mainly erosive bedrock beds, with the development of alluvial and flood plains in lower sectors and near the lakes, mainly over moraine systems and glaciofluvial-glaciolacustrine plains.

The lakes were selected according to their location relative to the PCCVC and following an ash deposition gradient as a measurement of volcanic impact. According to the gradient of the amount of ash deposited during the last PCCVC eruption, the lakes can be separated into higher-impacted lakes to the north and lower-impacted lakes to the south of the study area. The lakes Espejo, Espejo Chico, Correntoso, Ceferino, Bailey Willis, and Huillines, located to the East and closer to the volcano (Table 1), are in the area with the greatest deposition of ash (Fig. 1). Lake Villarino, located further north and slightly further from the volcano than the above-mentioned lakes (Table 1), received thinner ash deposits. On the other hand, the lakes Gutiérrez, Mascardi, Roca, and Guillelmo are located south and far from the CVPCC, distributed in an area with minimal ash contributions (Fig. 1).

Also, the lakes differ in the area and depth (Table 1), ranging from large and deep (area > 1 km^2; Z_{max} > 15 m), such as lakes Villarino, Espejo, Espejo Chico, Correntoso, Bailey Willis, Gutiérrez, Mascardi, Guillelmo, and Roca, to small and shallower

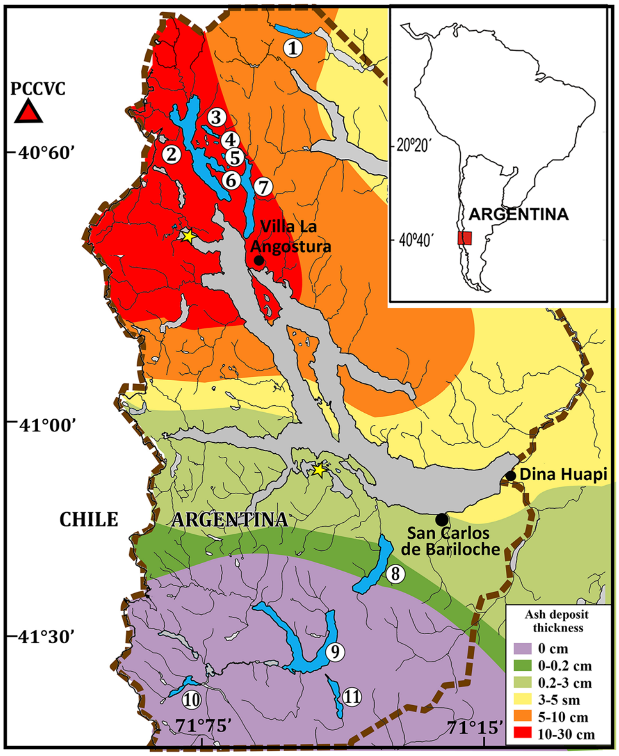

Fig. 1 Map of the study area with the location of the 11 sampled lakes in Northern Patagonia (Argentina): (1) Lake Villarino, (2) Lake Espejo, (3) Lake Espejo Chico, (4) Lake Bailey Willis, (5) Lake Huillines, (6) Lake Ceferino, (7) Lake Correntoso, (8) Lake Gutiérrez, (9) Lake Mascardi, (10) Lake Roca, (11) Lake Guillelmo. The locations of the Puyehue-Cordón Caulle complex (PCCVC, red triangle in the upper left margin) and the points of extraction of the sedimentary cores used to calculate background concentrations (yellow stars) are also indicated. The area delimited by the dashed line corresponds to the National Park Nahuel Huapi. The gradient of colors indicates the thickness of ash deposits from PCCVC (modified from Masciocchi et al. 2013)

Table 1 Physicochemical characteristics of lakes included in this study

Lake	Altitude (masl)	Area (km^2)	Z_{max} (m)	DV[d] (km)	[e]Water parameters				
					Secchi disk (m)	Temp (°C)[f]	pH[f]	Cond (mS/cm)[f]	DOsat(%)[f]
Villarino	925[d]	5.25[b]	> 100[b]	49	15.3	11.22	6.62	0.067	N/D
Espejo	750[a]	41.6	245[a]	36	19.5	12.38	6.76	0.034	94
Espejo Chico	750[a]	1.9[a]	68[a]	32	20	13.37	6.96	0.034	90
Ceferino	750[a]	0.1[a]	9[a]	36	3.5	16.08	6.36	0.113	49
Bailey Willis	750[a]	0.5[a]	30[e]	34	7	10.47	6.49	0.062	73
Huillines	750[c]	0.15[d]	~ 14[e]	35	4.5	19.66	6.84	0.061	91
Correntoso	750[a]	19.5[a]	> 100[c]	38	16	14.51	6.74	0.038	89
Gutiérrez	750[a]	16.4[a]	111[a]	91	19.7	12	6.64	0.068	86
Mascardi	795[a]	39.2[a]	218[a]	98	14	12.8	6.76	0.050	93
Roca	725[a]	4.94[a]	80[a]	92	9	10.94	6.5	0.036	79
Guillelmo	826[a]	5.4[a]	100[a]	102	19	12.39	6.76	0.063	91

DV distance from the sampling site to the Puyehue-Cordón Caulle volcanic complex, *Temp* temperature, *Cond* conductivity, *DOsat%* percent dissolved oxygen saturation

[a] Díaz et al. (2007)

[b] Pérez et al. (2007)

[c] Corno et al. (2009)

[d] Estimated with Google Earth Pro

[e] In situ water measurements

[f] Average values from the water column up to the maximum depth sampled

(area < 1 km^2; maximum depth Z_{max} < 15 m), such as Ceferino and Huillines. Lakes are oligotrophic to ultra-oligotrophic, with transparency values varying between a few centimeters to 20 m in depth (Markert et al. 1997; Modenutti et al. 1998). Deep lakes exhibit a warm monomictic thermal regime, with thermal stratification during late spring and summer, and thermocline being able to reach 30–40-m depth in very deep lakes (Modenutti et al. 1998). In the case of shallower lakes Ceferino and Huillines, the thermal regime is probably warm polymictic, as their waters can stratify and mix many times a year, favored by their shallow depth and the effect of the winds.

All the lakes are included within the Nahuel Huapi National Park and distributed throughout the SVZ of the Andean Range (Stern 2004). The climate is temperate cool with a mean annual temperature of around 11 °C, annual precipitation of 1500 mm, and prevailing westerly winds (Paruelo et al. 1998). The vegetation corresponds to the Andean-Patagonian temperate forest represented in the lakes' shores mainly by *Nothofagus dombeyi* and *Austrocedrus chilensis*.

2.2 Sample collection and analytical procedures

To assess the pollution status on a regional scale, the top 0–2 cm of undisturbed surface sediment from each lake was collected at two or three depths, defined as follows: coastal (sediment collection depth: < 5 m), intermediate (sediment collection depth: 5–15 m), and profundal (sediment collection depth: 16–85 m), during austral summer 2018 using a gravity corer. Sediment samples were placed into polyethylene bags, stored in a cooler in the field, and stored at 4 °C in the laboratory before analysis. The temperature, pH, conductivity, and dissolved oxygen concentration of overlying water were determined using a multiparameter probe (YSI 6600 V2).

The sediment samples were frozen and then freeze-dried until constant weight was achieved. Afterward, sediment samples were sieved with a 63-µm mesh sieve to obtain two-grain size fractions: silt–clay (< 63 µm) and sand (> 63 µm). The sediment silt–clay fraction was analyzed for trace element and organic matter (OM) contents. The OM was determined by loss on ignition (LOI_{550}) through the calcination of 0.5 g of dry sediment at 550 °C for 4 h, following Heiri et al. (2001).

The concentration of As, Br, Cr, Hg, Ni, and Zn were determined by Instrumental Neutron Activation Analysis (INAA) at the Laboratorio de Análisis por Activación Neutrónica (LAAN; Centro Atómico Bariloche, Argentina) in the < 63 µm sediment fraction, given its greater adsorbing capacity for elements and their role in the exchange of elements from the sediments to benthic organisms (Horowitz 1991; Amiard 1992). This procedure allows the correction of the natural variability of the particle sizes of sediments from a water body and to compare different depositional environments, such as coastal and deep environments (Herut and Sandler 2006). Moreover, in the studied lakes, the deposition of volcanic ashes in the sediments and the presence of coarse particles in the sites closest to the volcano are punctual events not representative of the typical fine sediments that characterize these lakes (< 63 µm represents 87–95% of bulk sediments in the two representative lakes used for reference, Table 2). Therefore, the dilution effect of race elements caused by those occasionally coarser particles was removed for the comparison between samples.

A mass ranging from 20 to 100 mg of sediment samples from the < 63 µm fraction was irradiated in the RA-6 nuclear research reactor for 6 h. These samples were transferred to fresh vials after irradiation to avoid interference of vial impurities and measured afterward using intrinsic High Purity Germanium (HPGe) detectors and a 4096 channel analyzer. Elemental concentrations were determined using the absolute parametric method. Analytical errors differ for each sample analyzed since they depend on their composition, varying from 7 to 14%. Certified Reference Materials NIST 2709a San Joaquin Soil and IAEA soil 7 were analyzed together with the samples for analytical quality control; the results are reported in Table S1. Measured concentrations coincided with certified values within the uncertainties.

2.3 Sediment quality

The quality of sediments and the ecological risks of trace elements in sediments were assessed by comparing the element concentrations determined in the < 63 µm fraction of the sampled sediments with three geochemical backgrounds and with sediment quality guidelines for freshwater ecosystems. The geochemical backgrounds used were the average continental crust shale values published by Turekian and Wedepohl (1961) and two representative local backgrounds. Given the lack of specific background levels for each sampled lake, two lakes with different proximity to the volcanic complex (and

Table 2 Mean concentration of As, Br, Cr, Hg, Ni, Zn, organic matter (OM) contents, and silt–clay proportions in < 63 µm surface sediments from each lake

	As	**Br**	**Cr**	**Hg**	**Ni**	**Zn**	**OM**	**Silt–clay**
Lake	Concentration (µg g^{-1})						(%)	(%)
Villarino	22.71	9.24	58.79	0.12	39.20	225.00	7.23	38.24
Espejo	13.88	9.88	7.81	0.10	8.23	108.87	2.76	25.34
Espejo Chico	22.20	16.56	20.82	0.14	17.90	146.00	5.54	38.17
Ceferino	14.19	10.46	120.70	0.11	78.85	95.20	4.58	45.61
Bailey Willis	13.40	9.06	27.93	0.14	22.07	113.20	4.36	33.07
Huillines	12.44	8.00	105.17	0.12	71.85	106.75	5.56	32.57
Correntoso	13.62	8.19	62.64	0.10	44.40	121.87	3.38	45.39
Gutiérrez[a]	224.00	25.80	67.54	0.30	35.20	164.00	13.39	79.06
Mascardi	17.06	29.40	68.92	0.10	52.20	218.50	15.55	89.17
Roca	12.33	19.09	138.44	0.17	86.37	126.60	21.30	96.71
Guillelmo	30.17	13.23	109.61	0.12	52.83	118.03	11.15	85.95
Selected local background 1[b]	12.77	8.52	14.09	0.12	11.97	96.7	-	86.72
Selected local background 2[c]	24.5	13.6	51.6	0.15	27.9	172.5	-	95.00
Baseline in several Patagonian lakes[d]	4.73–24.5	3.27–14.9	19.5–83.4	0.259–0.324	33.6–42.4	90.7–172.5	-	-
2011 PCCVC tephras[e]	14.9–15.7	4.43–4.92	2.24–9.10	-	-	95.4–104.6	-	-
Average shale[f]	13	4	90	0.4	68	95	-	-
	% of the sample in each guideline[g]							
< TEC	7	-	32	82	18	57		
≥ TEC < PEC	82	-	50	18	39	43		
≥ PEC	11		18	0	43	0		

TEC Threshold effect concentration, *PEC* probable effect concentration, local background concentrations, average shale concentrations, and range of concentrations in other Patagonian lakes are also shown

[a] Value based on one deep sample

[b] Local geochemical background calculated from the value at down-core from Lake Nahuel Huapi

[c] Local geochemical background calculated from the value at down-core from Lake Moreno

[d] Ribieiro Guevara et al. (2005); Román-Ross et al. (2002)

[e] < 63 µm fraction; Daga et al. (2014)

[f] Turekian and Wedepohl (1961)

[g] TEC and PEC values for each element are indicated in Fig. 3

therefore different volcanic impact), whose catchments are composed of different proportions of igneous and volcano-sedimentary lithologies, and for which baseline data are available, were chosen as local backgrounds, trying to reflect the different situations that could be found in the environments sampled. The concentrations used for this purpose corresponded to values determined in deep layers from one sedimentary sequence extracted at 55-m depth from a site in Lake Nahuel Huapi close to the PCCVC and to another extracted at 25-m depth in Lake Moreno that received less volcanic impact (Ribeiro Guevara et al. 2005). In both cases, the volcanic ashes levels in the sequences were avoided.

For assessing the quality of sediments for benthic organisms, "consensus-based" sediment quality guidelines (SQGs) were used (Macdonald et al. 2000). According to these guidelines, the threshold effect concentration (TEC) and the probable effect concentration (PEC) are defined. If the element concentrations measured in the sediment are below TEC, elements are not expected to have any adverse effects on aquatic organisms. However, if the element concentrations in the sediment are above PEC, toxic effects are likely to occur, whereas concentrations between PEC and TEC indicate that adverse biological effects are expected to occur occasionally. Such definitions are based on the premise that the probability of toxic effects from exposure to a given chemical increases with the concentration of that substance in sediments (Macdonald et al. 2000).

Also, two indices were calculated to assess the environmental quality of sediments: the enrichment factor (EF) and the index of geo-accumulation (I_{geo}).

The enrichment factors are usually determined to understand whether the trace elements are present in high concentrations relative to a preindustrial regional reference level consequent to anthropogenic pollution (Dung et al. 2013). In the present study, this index was used to evaluate if volcanic eruptions, as an external sporadic source of elements, can affect the baseline compositions, and to detect signs of incipient anthropogenic contamination. The EFs were calculated as follows:

$$EF = (M/X)_{sample}/(M/X)_{background} \quad (1)$$

where M is the evaluated element, X is a geochemical tracer (reference element) that does not account for enrichment by a specific source (e.g., anthropic contamination) allowing the normalization to consider natural variability, and $(M/X)_{\mathrm{sample}}$ and $(M/X)_{\mathrm{background}}$ are the ratios of the evaluated element and the reference element in the surface and background sediments, respectively (Sutherland 2000).

Because the EF is highly influenced by the natural variability of the reference material and by physical–chemical alterations of the elements in the materials of the earth's crust (Reimann and De Caritat 2005), an adequate normalizer must be chosen based on site-specific criteria and according to the purpose of assessment. Rare earth elements (REE) are suitable for geochemical studies and provenance composition analysis of the material due to their stability against biogeochemical processes, no fractionation during sedimentation, low solubility, and relative immobile in surface and aqueous environments (McLennan 1989; Fonseca et al. 2021). For this study, samarium (Sm) was chosen as the normalizer as it is an element that is not affected by surface geochemical processes and has high analytical precision and low detection limit with the AANI technique.

The degrees of metal "contamination" were classified according to criteria proposed by Sutherland (2000). An EF < 2 indicates zero to minor contamination, 2–5 indicates moderate contamination, 5–20 indicates significant contamination, 20–40 indicates very high contamination, and > 40 indicates extremely high contamination.

To quantify the extent of trace element "contamination" associated with the sediment, the index of geo-accumulation (I_{geo}) introduced by Müller (1969) was used and defined by the following equation:

$$I_{geo} = log_2\, C_n/1.5\, B_n \quad (2)$$

where C_n represents the measured concentration of metal (n) in samples (μg g^{-1}) and B_n represents the geochemical background concentration (μg g^{-1}) of the element (n). Factor 1.5 is used to account the variability in background values. The I_{geo} display in seven classes, namely class 0 ($I_{\mathrm{geo}} \leq 0$), uncontaminated; class 1 ($0 < I_{\mathrm{geo}} < 1$), uncontaminated to moderately contaminated; class 2 ($1 < I_{\mathrm{geo}} < 2$), moderately contaminated; class 3 ($2 < I_{\mathrm{geo}} < 3$), moderately to heavily contaminated; class 4 ($3 < I_{\mathrm{geo}} < 4$), heavily contaminated; class 5 ($4 < I_{\mathrm{geo}} < 5$), heavily to extremely contaminated; and class 6 ($I_{\mathrm{geo}} \geq 5$), extremely contaminated (Müller 1969). For both the EF and the I_{geo}, the geochemical concentration determined at the down-core from both Lake Nahuel Huapi and Lake Moreno was used.

2.4 Statistics

Statistical analysis was performed using SigmaStat 10.0 statistical software. Shapiro–Wilk statistical tests were employed to evaluate the normality of the data. As the data for sediments deviate from normal distributions, Spearman correlation analysis was implemented to determine the relationship among the elements and between elements and environmental variables. Sediment grain size (as %silt–clay), organic matter (as %OM), distance to PCCVC (as DV), and physicochemical parameters of water (i.e., depth of sampling, the water temperature at sampling depth, transparency, percent dissolved oxygen saturation, conductivity, and pH) were used and defined as "environmental variables" (Table 1).

3 Results and discussion

3.1 General characteristics of lake surface sediments and water

The mean physicochemical parameters of water and surface sediments of the lakes are shown in Tables 1 and 2. The sediments of lakes closest to the PCCVC (Fig. 1), located north (Villarino) and east of the volcano (Espejo, Espejo Chico, Correntoso, Bailey Willis, Huillines, and Ceferino), were predominantly composed of sands (average percentage > 60%), whereas the sediments from the lakes located to the south and further from the influence of the PCCVC (Gutiérrez, Mascardi, Guillelmo, and Roca) were mainly silt–clay (average percentage > 70%) and also differed between lakes near and far from the volcano, with lower and higher %OM, respectively (Table 2). The %OM was positively correlated with the %silt–clay (Table 3), with OM contents in the silt–clay fraction varying between 1.5 and 25% (Fig. 2). Consequently, both %silt–clay and %OM positively correlated with the distance to the volcano (Table 3). These results are consistent with the grain size gradient expected in the tephras dispersed by the PCCVC in the 2011 eruption and deposited in the lakes: decreasing coarse particles amounts as the volcano distance increases (Wilson et al. 2013) (Fig. 1). Lower OM content in the silt–clay fraction of lakes closer to PCCVC could also reflect the presence of fine volcanic components in northernmost lakes (Fig. 2). Grain size and OM are key factors that influence the content and availability of metals and other trace elements in sediments parameters (Singh et al. 1999; Zhang et al. 2014). The larger surface-to-volume ratio of the smaller sediment particles determines higher adsorption capacity and therefore higher concentration of metals (Loring and Rantala 1992).

As expected, a general pattern of increase in the proportion of silt–clay sediments was observed in the samples from shallower to deeper positions of each lake (Fig. 2). Finer particles dominate in deep water sediments, where continuous accumulation prevails, while surface processes and dynamic processes keeping materials suspended in water bodies are generally more active near the coast than away from it (Wetzel 2001).

3.2 Trace elements in lake surface sediments

Mean trace element concentrations in < 63 µm surface sediments are presented in Table 2. This is the typical grain size fraction that characterizes the lakes of the region, and because of its higher interaction with benthic organisms, it is the one of the greater interest in this study. Different distribution patterns were observed for each element when correlated with environmental variables.

Higher As concentrations were found in sediment samples collected in the deepest zones, where accumulation processes prevail over particle suspension, predominantly in the deepest lakes (e.g., Espejo, Gutiérrez, Mascardi, and Guillelmo) with a particularly high value in Lake Gutiérrez (Fig. 3). A positive correlation between As concentration and sampling depth was found, whereas temperature, pH, and dissolved oxygen were negatively correlated with As (Table 3).

Table 3 Spearman correlation coefficient (rho) for heavy metals and environmental variables

	As	Br	Cr	Hg	Ni	Zn	OM	Silt-Clay	DV	Depth	Temp	pH	DO	Cond
Br	0.29													
Cr	-0.12	0.24												
Hg	0.05	-0.08	0.17											
Ni	-0.25	0.23	**0.95****	0.18										
Zn	0.35	**0.55****	0.07	0.01	0.09									
OM	0.095	**0.70****	**0.54****	0.06	**0.45***	**0.49***								
Silt-Clay	0.36	**0.39***	**0.48***	0.03	**0.42***	0.30	**0.64****							
DV	0.25	**0.38***	**0.69****	0.09	**0.58**	**0.44***	**0.72****	**0.78****						
Depth	**0.69****	0.21	-0.10	0.09	-0.13	**0.38***	-0.06	0.37	0.15					
Temp	**-0.68****	-0.21	0.19	-0.01	0.21	-0.33	0.02	**-0.47***	-0.15	**-0.86****				
pH	**-0.40***	-0.07	-0.10	-0.09	-0.14	-0.27	0.05	-0.26	-0.08	**-0.67****	**0.72****			
DO	**-0.43***	0.08	-0.03	-0.22	-0.04	-0.12	0.21	-0.04	0.06	**-0.50****	**0.62****	**0.84****		
Cond	0.24	-0.06	0.37	0.19	0.25	-0.02	0.06	0.03	0.30	-0.01	-0.14	-0.36	**-0.56****	
Secchi disk	0.28	0.11	**-.40***	0.18	**-0.52***	0.07	-0.06	-0.05	**0.47***	0.35	-0.14	0.16	**0.47***	**-0.52***

Values in bold indicate significant correlations

*Correlation is significant at 0.05 level

**Correlation is significant at 0.01 level

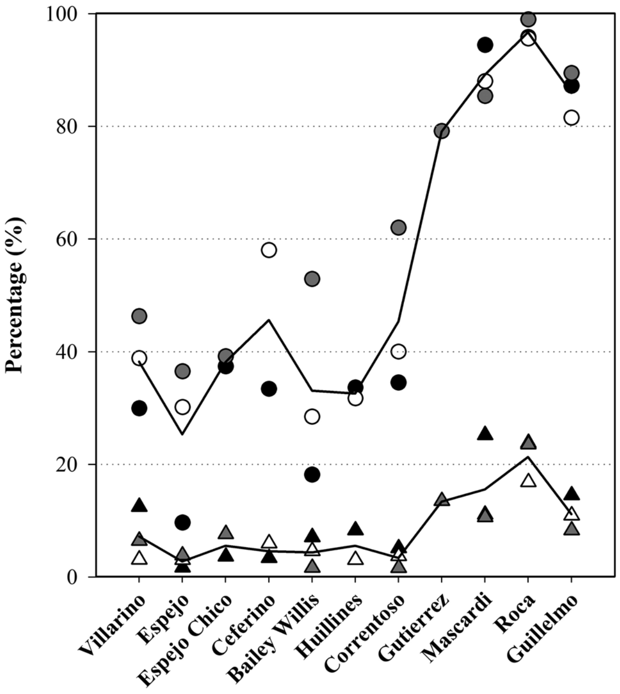

Fig. 2 Proportion (%) of silt–clay fraction (circles) and organic matter (triangles) in coastal (black), intermediate (gray), and profundal (white) surface sediment samples in each lake. Black continuous lines represent the average values of each lake

Arsenic concentrations in most samples were within the ranges recorded in low anthropic-impacted Patagonian lakes influenced by volcanic activity (e.g., Ribeiro Guevara et al. 2005) and are comparable to the average values for Earth Crust shale (Table 2). However, As concentrations determined here, even the local background values, are comparable to levels recorded in sediments associated with moderate to high contamination by urban and industrial effluents in northern hemisphere water bodies (Yang and Rose 2005; Gawel et al. 2014). Moreover, the extremely high As concentration found in Lake Gutiérrez (224 µg g^{-1}) is in the range of values recorded in sediments from a watershed in the south-central Puget Sound region (Washington State), heavily contaminated by a metal smelter (Gawel et al. 2014). It is important to note that As concentration profiles in sedimentary sequences frequently show sharp peaks in layers near the surface caused by As migration due to redox gradients (Boyle 2001). Similar As levels have already been recorded in surface sediments extracted in the study area, in an 85-m-deep sediment sequence from the nearby Lake Moreno (250 µg g^{-1}; Ribeiro Guevara et al. 2005); therefore, redox processes cannot be ruled out.

According to the lakes' location regarding PCCVC, no relationship between sediment As concentration and distance to the volcano was found. Even though values were variable, the highest As contents were detected among the furthest lakes to PCCVC. It is noteworthy that measurements of As in 2011 PCCVC tephras do not exceed 16 µg g^{-1} (Table 2), whose presence in the sediments of the lakes closest to the volcano could be causing a dilution effect on the arsenic concentrations.

Bromine was positively correlated with %OM, %silt–clay, and the distance to PCCVC (Table 3), consistent with the highest Br concentrations found in sediments of lakes more distant to the volcano (i.e., Gutiérrez, Mascardi, Guillelmo, and Roca; Table 2). Volcanic events are a known source of halogen elements to the environment (Bureau et al. 2000; Oppenheimer et al. 2006), and Br release has been associated with the 2011 PCCVC eruption (Bubach et al. 2012), while Br measured in pyroclastic material from the same eruption (4.43–4.92 µg g^{-1}; Table 2) were lower than concentrations obtained in sediments in this work. Since volcanic ashes have lower OM and Br than lacustrine sediments (Daga et al. 2014; Ribeiro Guevara et al. 2019), lower Br and OM are expected in lake sediments with higher ash deposition than in less impacted lakes, as observed here. Moreover, previous studies have identified a close association between OM and Br in lacustrine sediments (Ribeiro Guevara et al. 2019), which might be the cause of the relationship observed in this study. Bromine concentrations in most samples are in line with concentrations measured in sedimentary sequences from other lakes in the study area (e.g., Morenito, Moreno, Nahuel Huapi, and Traful; Ribeiro Guevara et al. 2005, 2019).

Chromium and Ni had a similar spatial distribution pattern. The highest concentrations were found in the deepest sample from Lake Roca (191.95 and 111.30 µg g^{-1}, respectively), more than ten times higher than local background levels (14.09 and 11.97 µg g^{-1}, respectively; Fig. 3), and nearly twice the average Earth shale values (Table 2). Chromium and Ni correlated positively with %OM, %silt–clay, and water transparency (rho < 0.6), and also with DV (rho = 0.68). Therefore, higher concentrations were observed in lakes furthest from the volcano. Since lower Cr concentrations were reported in volcanic ashes (2.24–9.10 µg g^{-1}, Table 2), a dilution effect can be also acting in this case. On the other hand, higher Cr and Ni were also found in lakes with low transparency but closest to the volcano, such as the shallower lakes Ceferino and Huillines. These two small lakes had concentrations of Cr and Ni in the range of the most distant lakes (Table 2), suggesting that other variables not considered in this work could be implied. For instance, Lake Huillines receives a large contribution of allochthonous organic matter through the riparian vegetation, dominated by *Nothofagus dombeyi*, while Lake Ceferino is dominated by the emergent macrophyte *Schoenoplectus californicus*. It has been shown that the inputs of terrestrial organic matter promote the accumulation of metals in the sediments of estuaries (Jokinen et al. 2020), while leaf litter decomposition was particularly proven to be an important source of elements to aquatic ecosystems (Juárez et al. 2016). According to Juárez et al. (2016), particularly the leaf of *N. dombeyi*

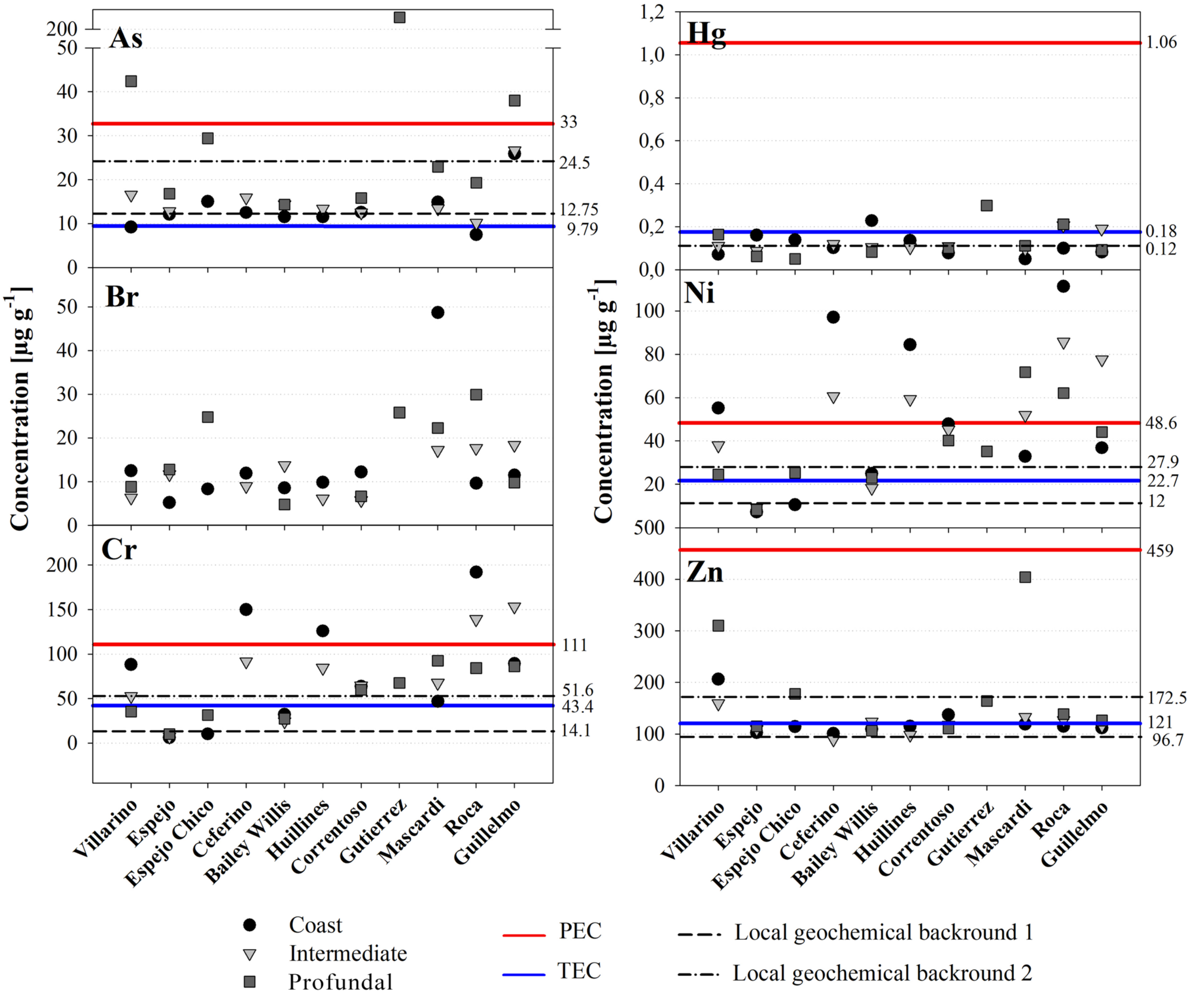

Fig. 3 Concentrations of As, Br, Cr, Hg, Ni, and Zn in surface sediments from sampled lakes. The PEC (red horizontal line) and TEC (blue horizontal line) values proposed by MacDonald et al. (2000), and two local geochemical background values ((1) Lake Nahuel Huapi, (2) Lake Moreno) are also indicated

and *S. californicus* showed a high capacity to concentrate Cr during microbial decomposing. Therefore, leaf litter decomposition may favor the higher Cr concentrations observed in the mentioned shallow lakes. On the other hand, an unusually low percent dissolved oxygen saturation was measured in Lake Ceferino waters (as low as 49%, Table 1) compared to the high saturations commonly described for Patagonian oligotrophic lakes and measured in the other studied lakes. It is known that the fate and mobility of Cr in surface sediments are controlled by redox reactions; therefore, the different redox conditions expected in Lake Ceferino compared to the other lakes may influence the highest Cr concentrations recorded in its sediments. Chromium and Ni positively correlate with each other, but not with the other elements (Table 3), suggesting a common origin of these two elements in the sediments and similar geochemical behavior, evidenced in their similar spatial distribution patterns. This behavior was also observed by Zhang et al. (2016), although in their investigation the higher Cr and Ni concentrations were associated with an anthropic origin. Meanwhile, Liao et al. (2017) explained the strong Cr-Ni correlation found by geological weathering. In more than half of the samples measured in the present study, Ni concentrations exceed the levels recorded for other lakes in the area (Table 2). Nickel can be deposited in sediments by processes such as precipitation, complexation, and adsorption on clay particles and by absorption by biota and was also observed to be associated with OM in other studies (Barałkiewicz and Siepak 1999; Cempel and Nikel 2006). The positive correlation of Ni concentrations with %OM, silt–clay proportion, and Cr concentrations help to understand the observed spatial distribution of these elements in lake surface sediments.

Zinc concentrations were positively correlated with %OM, DV, and sampling depth, although with a low linear model fit (rho = 0.4–0.5, Table 2). Zinc concentrations are in the range of concentrations recorded in lake sediments from the study area (e.g., lakes Nahuel Huapi, Traful, and Moreno; Ribeiro Guevara et al. 2005) and are mostly higher than those concentrations recorded in volcanic ashes (95.4 to 104.6 μg g^{-1}; Table 2). However, all values are near the lower limit of the concentration range recorded for sediments moderately contaminated by urban and industrial effluents in lakes in the northern hemisphere (Camarero et al. 2009). On the other hand, in profundal samples of lakes Villarino and Mascardi, Zn concentrations were 310 μg g^{-1} and 404 μg g^{-1}, respectively, close to the concentrations recorded in a shallow lake located near one of the most important urban centers in the region, the Lake Morenito (Ribeiro Guevara et al. 2005). It is said that volcano ashes may facilitate the incorporation of elements such as As, Cr, and Zn into aquatic ecosystems (Ruggieri et al. 2011; Perez Catán et al. 2016). For instance, an increase in the concentration of Zn was observed in the water column of Lake Nahuel Huapi, after the 2011 PCCVC eruption, possibly caused by the release of Zn from the deposited volcanic ashes (Perez Catán et al. 2016); however, no impact on the aquatic biota was observed (Montañez et al. 2018). It is worth noting that a positive correlation was found between Zn and Br, suggesting a common source or similar geochemical processes involved in their behavior. Also, Br and Zn concentrations were positively correlated with the OM contents in the samples, evidencing the great influence of OM in the distribution of these elements in surface sediments of lakes.

Mean Hg concentrations in the studied lakes sediments ranged between 0.1 and 0.3 μg g^{-1} (Table 2). Mercury is a pollutant associated with global atmospheric transport and wet deposition usually showing higher values in modern sediment layers than in pre-industrial ones (Lent and Alexander 1997). Based on the analysis of sedimentary sequences from six lakes in the Lake Nahuel Huapi National Park, it was previously established a range of Hg concentrations between 0.08 and 0.2 μg g^{-1} for pre-industrial times and between 0.17–0.32 μg g^{-1} for modern times (Ribeiro Guevara et al. 2005). According to this, almost all lakes analyzed in the present work had Hg concentrations in the range of pre-industrial levels, except for Lake Gutiérrez which presented the highest Hg concentration (0.3 μg g^{-1}), corresponding with modern concentrations but still at a low level. No correlations between Hg concentrations and environmental variables were found (Table 3). Although OM has been pointed out as an important regulator of the dynamic of Hg in lake sediments (Kainz and Lucotte 2006; Sanei and Goodarzi 2006; Teisserenc et al. 2011), no relationship was found between them in the present study. The lack of correlation between Hg and OM has been interpreted as Hg inputs being independent of the productivity of the lakes and soil erosion and not related to redox gradients either (Daga et al. 2016). High levels of Hg previously observed in historical lake sedimentary sequences in the study area have been associated with regional fire episodes and volcanic activity, both very frequent phenomena in the region (Ribeiro Guevara et al. 2010; Daga et al. 2016).

3.3 Probability of toxic effects

Comparison with sediment quality guidelines has become a very common approach as a first step for assessing environmental impacts. Given that the probability of toxic effects resulting from exposures to a given chemical increases with the concentration of that substance in sediments (Macdonald et al. 2000), the quality of sediments for benthic biota was evaluated by the comparison of metal concentrations with the PEC and TEC limits established in Macdonald et al. (2000). PEC and TEC values for each element are indicated in Fig. 3.

According to the TEC and PEC (Fig. 3), three of the eleven lakes have average surface sediment concentrations that exceed the PEC for As (lakes Villarino, Guillelmo, and Gutiérrez), four lakes exceed the PEC for Cr (Ceferino, Huillines, Roca, and Guillelmo), six lakes exceed the PEC for Ni (Villarino, Ceferino, Huillines, Mascardi, Roca, and Guillelmo), while for Hg and Zn, mean concentrations were below the PEC for all lakes (Table 3). When looking at concentrations at each sampled depth (Fig. 3), profundal samples were the reason for the above-PEC values for As, while Cr concentrations above the PEC were recorded in coastal and intermediate samples (Fig. 3). Nickel appears as the element of greatest concern, registering concentrations greater than PEC in 43% of the samples. Most samples had concentrations between TEC and PEC and even below TEC (Table 2), indicating a moderate to no probability of adverse effects in biota (71% of the samples for As, 43% for Cr, 18% for Hg, 25% for Ni, and 38% for Zn). Mercury and Zn levels are the less harmful with 82% and 57% of the samples, respectively, being below TEC. Nonetheless, the mere fact of exceeding the SQG values does not necessarily guarantee the occurrence of deleterious ecological effects, unless they are also coherent with regional background data (Chapman et al. 1999; Roach 2005). For instance, some investigations found element concentrations in surface sediments above guideline values although they did not exceed the regional background levels (Farkas et al. 2007) concluding that background values could be more reliable than SQG. Given the lack of specific background values for the studied lakes, the deep strata of two sedimentary cores, one from Lake Nahuel Huapi and one from Lake Moreno were used in this study to obtain baseline concentrations. Except for As, background values from Lake Nahuel Huapi for all the analyzed elements are quite less than the TEC (Fig. 3), while background sediment concentrations from Lake Moreno are mostly between TEC and PEC (Table 2; Fig. 3). This variation in background values is well reflected in the range of baselines determined for several North Patagonian lakes (Table 2) indicating that natural concentrations of elements can vary regionally in response to specific geological features of the catchment. Despite the varying background levels, in this work it was shown that the concentrations of As, Cr, and Ni in the sediments of certain lakes are far above the PEC and also above the range of natural concentrations for several lakes in the region (Table 2). The greatest concern falls on Cr and Ni levels, since, unlike As, which only exceeds the PEC value in deep samples (> 50-m depth) where benthic organisms are unlikely to inhabit, Cr and Ni exceed the PEC in coastal samples (< 5-m depth) were most organisms live. According to this, the harmful effects on sediment-dwelling and aquatic organisms have the potential to occur frequently in the lakes Ceferino, Huillines, Roca, and Guillelmo.

3.4 Contamination assessment

To make a more reliable evaluation of the environmental quality of the sediments, indices such as the EF and the I_{geo} are usually used, which take into account the natural variation of sediments by "normalizing" the content of an element in the sample relative to a conservative lithogenic element assumed to be exclusively influenced by crustal sources. This section first describes the results obtained using the concentrations from the Lake Nahuel Huapi sedimentary core as baseline, and then a comparison is made with the indices obtained using the baseline concentrations from Lake Moreno.

Mercury showed the lowest EFs ($EF < 1$) falling into the category of "minimal enrichment" for the entire region, indicating, as was mentioned, that sediments from the analyzed lakes are not "contaminated" with Hg (Fig. 4). All lakes presented "minimal" to "moderate enrichment" for As, except in Lake Gutiérrez with an $EF = 21$ indicating "very high enrichment." Chromium and Ni presented "significant enrichment" in lakes Ceferino, Huillines, and four southern lakes, with "very high enrichment" for Cr in Lake Roca. Bromine and Zn were in general "minimal to moderate enriched," with higher EF values for Br in lakes Mascardi and Roca and higher for Zn in lakes Villarino, Mascardi, and Roca. It is generally accepted that EF values between 0.5 and 1.5 indicate that the metal is entirely from crustal materials or natural processes, whereas values of $EF > 1.5$ are considered to indicate that an important proportion of trace metals is delivered from non-crustal materials, for example, biota and/or pollution drainage (Zhang and Liu 2002). According to this, only the sediments collected in lakes Espejo, Espejo Chico, and Bailey Willis could be considered as "natural" enriched, whereas most of the lakes would receive some external contribution of elements. In the studied area, the volcanic activity could be considered an external but natural contribution to the "lake system". Volcanic eruptions release into the atmosphere pyroclastic products and gases containing various trace elements that eventually reach water bodies and settle in their sediments (Witham et al. 2005) causing higher regional enrichments than expected. However, the presence of volcanic ash from the latest PCCVC eruption in the sediment sample seems to cause a dilution effect on the concentrations of elements when compared to sediments without ash, including those elements considered of volcanic origin, and that should be taken into account when drawing conclusions about enrichment factors and in future monitoring. On the other hand, higher OM in lakes far from the volcano or allochthonous inputs of elements, driven by terrestrial OM (e.g., leaf litter), may contribute to the higher enrichments found. Aleksander-Kwaterczak and Ciszewski (2020) observed that the decomposition of the leaves lowers the pH of the soil increasing the mobility of metals. This could be occurring in lakes Ceferino and Huillines, explaining the higher enrichments obtained in their sediments.

The mean I_{geo} of each element showed the following decreasing gradient: Cr (1.29) - Ni (1.03) - Br (−0.12) - As (−0.14) - Zn (−0.14) - Hg (−0.72). Arsenic, Cr, and Ni were the metals with I_{geo} values higher than 1 in specific lakes, suggesting moderately contaminated sediments in lakes Villarino, Correntoso, Gutiérrez, Mascardi, and Guillelmo ($1 < I_{geo} < 2$), moderately to heavily contaminated sediments in lakes Ceferino, Huillines, and Roca ($2 < I_{geo} < 3$), and heavily contaminated sediments in Lake Gutiérrez ($I_{geo} > 3$). Uncontaminated to moderately contaminated sediments were the classifications for Hg, Br, and Zn at all lakes (Fig. 4).

As a general pattern, deep lakes located near the PCCVC have minimal to moderate enrichment/contamination by the metals analyzed, while lakes far from the PCCVC and shallow lakes Ceferino and Huillines have significant to high enrichment/contamination, consistent with the idea of dilution effect pointed out. It is worth noting that these indices are widely used to assess the degree of contamination from anthropogenic sources (Dung et al. 2013), while in this study, they were used to assess a "natural" source such as a volcanic eruption, which, due to its occasionality, was analyzed here as an external source to the natural environment. However, in either case, these indices should be used with caution, knowing their limitations. For example, Reimann and Caritat (2005) showed that different patterns of contamination can be reached depending on the background values and the reference element used for the calculation of the EFs. Given the natural variation expected in particular ecosystems, it is usually recommended to use local background (instead of average continental crust) and a reference element with low regional variability, as was attempted in this work. Considering the observed variability of background values between lakes, the EF and I_{geo} were calculated using the background concentrations of Lake Nahuel Huapi and Lake Moreno, with lower and higher elemental background concentrations, respectively (Table 2), to get an idea of the variability in contamination assessments by using different local background concentration sets (Tables S2 and S3). As

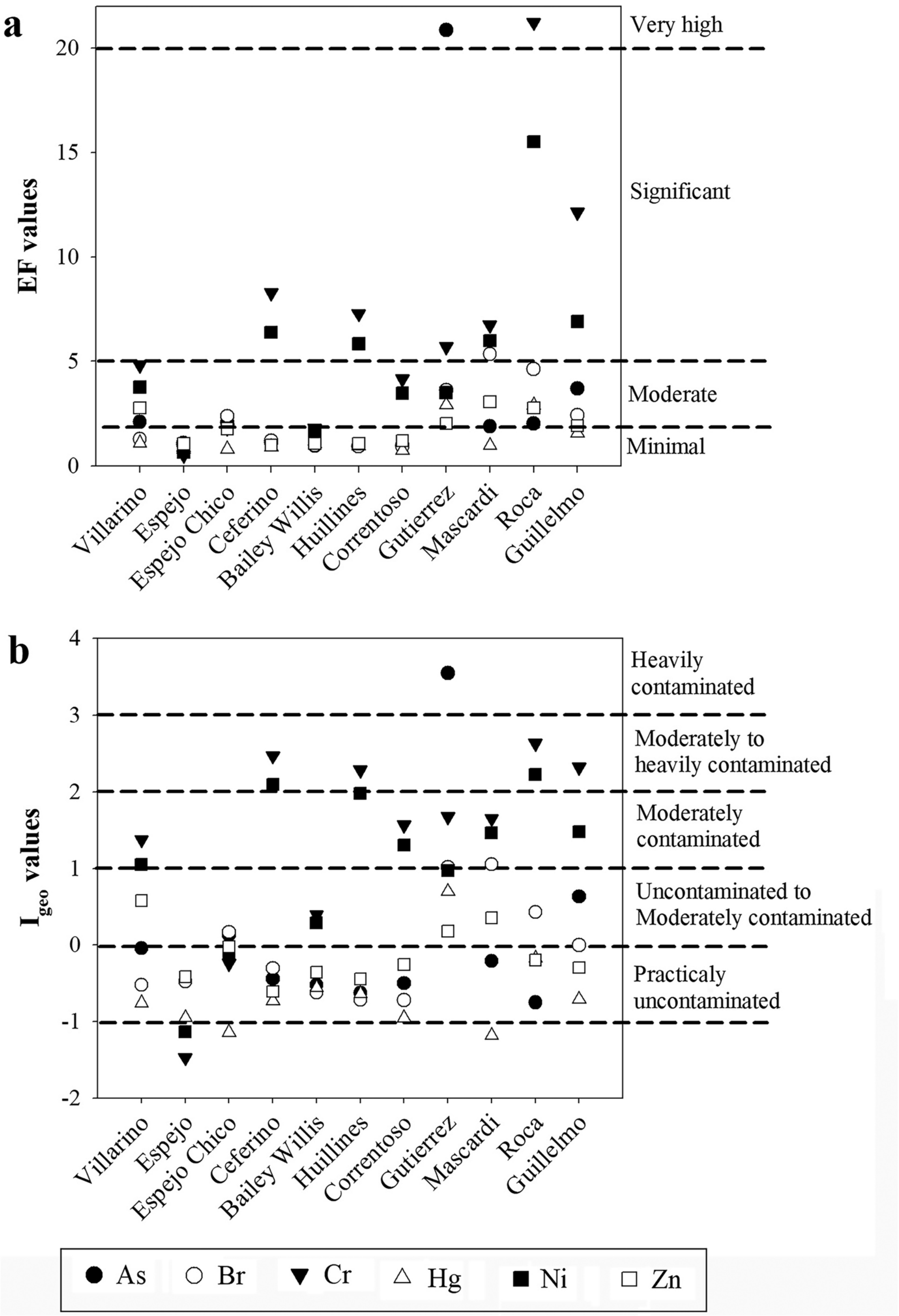

Fig. 4 **a** Mean enrichment factor (EF) and **b** index of geo-accumulation (I_{geo}) calculated for each element and lake using Lake Nahuel Huapi background. The category of enrichment/contamination for each index, following Sutherland (2000), is indicated

expected, using Moreno background levels, most EFs and I_{geo} values dropped one category, being the maximum degree of enrichment "significant" and the maximum degree of contamination "moderately to heavily contaminated." This highlights the necessity of considering lake-specific background values for this kind of evaluation, although diverse results have been observed even using very locally calculated backgrounds (Aleksander-Kwaterczak et al. 2021). Despite these methodological limitations, present results show consistent trends for some elements, as is the case of Cr and Ni in the lakes Ceferino, Huillines, and Roca. Another aspect to be considered in future research is the variability due to local biogeochemical conditions, such as redox conditions, OM sources, and biological processes, which have been seen to influence the distribution of certain elements and consequently the resultant indices values (Reimann and Caritat 2005). In the particular case of the environments influenced by volcanic activity, in this study, the effect of the volcanic ash in sediments was observed on the concentrations of certain elements. Since volcanic ashes have lower concentrations of most elements than the geological background (Table 2), the observed effect was a dilution of the total concentrations of the sediment, impacting the patterns of enrichment/contamination of the area. However, other physical–chemical effects of ashfall should be evaluated in future works. Ash deposition on sediments can act as a barrier that prevents the interaction between lake sediments and the aqueous interface above the sediment, limiting elements to the geological compartment and modifying their effect on the benthic habitat. On the other hand, ash deposits can cause changes in the physical–chemical conditions of the surface sediments (such as oxygen reduction or anoxia, pH variations) favoring the mobilization of certain elements towards the water column. Therefore, the interaction between the lake sediments, the deposited ashes, and the interface water should be addressed in conjunction with elemental concentrations to better understand potential contamination risks in this region.

4 Conclusions

This is the first work in the area in assessing the relative environmental quality and potential impact on the biota of surface sediments of different Andean-Patagonian lakes regarding potentially toxic trace elements of global importance in the context of volcanic activity. The effect of volcanic eruptions was revealed through the dilution of element concentrations in sediments of lakes subjected to a greater contribution of volcanic ash. Although the lakes belonging to the Nahuel Huapi National Park could be expected to be low anthropic-impacted, almost unpolluted concerning trace metals and metalloids, the different approaches used in this work indicated concentrations of some elements at levels considered polluting or risky for the aquatic biota. According to the consensus-based SQGS, the concentrations of As, Cr, and Ni have the potential to cause harmful effects frequently on sediment-dwelling organisms in the lakes Villarino (because of As), Ceferino (Cr and Ni), Huillines (Cr and Ni), Gutiérrez (As), Roca (Cr and Ni), and Guillelmo (As, Cr, and Ni). Regarding the sources and level of contamination, according to the EF and I_{geo} indices, deep lakes located near the volcanic complex have minimal to moderate enrichment/contamination, consistent with the dilution effect caused by volcanic ashes, while lakes far from the volcano and the shallow ones Ceferino and Huillines have a significant to high enrichment/contamination level.

In general, the physical–chemical conditions of the oligotrophic Andean-Patagonian lakes (e.g., low pH, high oxygen saturation, low water temperature, thermal stratification) favor the stability/immobility of most elements in the sediments; however, catastrophic events such as volcanic eruptions, slides of sediments, or even anthropic activities could change those conditions and turn the elements available to the aquatic organisms. Special attention deserves shallow lakes such as Ceferino and Huillines, with higher water temperatures and likely higher microbial activity and higher organic matter in the system, and therefore different biogeochemical dynamics, which make them more vulnerable to eventual entries (natural or anthropic) of trace elements.

In summary, the results of this study suggest a dilution effect of the volcanic ashes on the concentrations of elements in sediments closest to the PCCVC and therefore a higher metal enrichment, contamination, and risk for biota in lakes furthest from the volcano. This effect would be temporary and recurrent in the area since, with time, the return to "normal" sedimentation conditions in the lakes buries the strata of ashes deposited, as well as the direct effect exerted by the ashes. Eventually, a new eruption and ash deposition would once again affect the concentrations of the elements in the lake's sediments, and so on, in a cyclical manner. Present results warn about the vulnerability of lakes Ceferino, Huillines, Gutiérrez, and Roca to future sources of contamination, particularly of Cr, Ni, and As. This information will be an important starting point for future lake monitoring, as well as for investigations regarding trace element dynamics and biogeochemical processes in freshwater systems impacted by volcanic activity.

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Availability of data and material The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare no competing interests.

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