

Characterization of freshwater changes in lakes of Nahuel Huapi National Park produced by the 2011 Puyehue–Cordón Caulle eruption

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Abstract This work supplies a characterization of the chemical properties, including data of dissolved major and minor components in surface and pore water collected in Argentinean lakes surrounding the impacted area of Puyehue–Cordón Caulle volcanic complex, in the 2011 eruption. The principal component analysis and Pollution Load Index were used for the identification of water changes by volcanic ashes deposited throughout 1 year of eruption. The element content between water column and pore water provided a direct evidence of the potential dissolution of the element. Many chemical transformations, after the pyroclastic material contacted with the freshwater, were observed such as large pH changes from 3.2 to 8.1, electrical conductivity of 28.9 to 457 $\mu\text{s}/\text{cm}$, and redox potential of 171 to 591 mV. The maximum concentrations measured of F, Al, and Hg were 600, 40, and 0.0382 $\mu\text{g}/\text{L}$ respectively. These concentrations in water column were lower than the limit of aquatic life protection for chronic toxicity. The Pollution Load Index indicated very low pollution for sites far away from the volcano and moderated pollution in closely sites. The processes were stabilized at the end of the monitoring, 1 year after the eruption.

Keywords Puyehue–Cordón Caulle · Elements · Volcanic ash

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Introduction

The volcanic ash deposition on aquatic ecosystems can lead to several physical, chemical, and biological phenomena (Witham et al., 2005 and its references). The recently deposited ash has many adsorbed elements which are highly soluble; those could be leached to the aquatic environment. The weathering of the elements and the absorbed acids can cause a decrease in the drinking water resources due to changes in the pH and increases in salinity and potentially toxic element contents.

Volcanic eruptions are a well-known source of elemental input for the environment (Lee, 1996). The information about weathering and transport from volcanic ash are generally available through laboratory leaching experiments (Aiuppa et al., 2000, Cordeiro et al., 2012; Durant et al., 2012; Olsson et al., 2013). There are only a few monitoring studies made on surface and ground water after volcanic eruptions like the Mount St. Helens, Washington, in EEUU, and the Mount Nyamuragira, Virunga National Park, in D.R. Congo (Smith et al., 1983; Mc Knight et al., 1988; Lee, 1996; Cuoco et al., 2013). The physical, chemical, and biological characteristics were measured taking into account the environmental conditions, when the ash comes into the water bodies. The identification of a significant impact on water quality associated with the eruption included the lower pH; increases of F and Cl, SO₄, Na, Ca and potentially toxic metals (e.g., Al, Mn⁺, Cd⁺, Pb); and particulate matter load. In many cases, the water's composition significantly exceeds the World Health Organization (WHO) drinking water standards. Also, Morgan and Gislason (2008) suggested that the deposition of volcanic ash can both fertilize and/or poison aqueous environments, causing significant changes to surface water chemistry and biogeochemical cycles.

The impacts of the pyroclastic products on freshwater bodies of the North Patagonia, Argentina, are from the southern volcanic zone (SVZ) in the Chilean Andean Range. The SVZ is an active volcanic region with a high historic eruptive frequency with some early twenty-first century events such as Copahue in 2013, Puyehue–Cordón Caulle volcanic complex (PCCVC) in 2011, Llaima in 2009, Chaitén in 2008, and also Hudson in 2011 (Petit-Breuilh Sepúlveda, 2004; SERNAGEOMIN, 2013). Reports of identification and characterization of distal tephra deposits from different volcanic sources in lacustrine sedimentary sequences from Patagonian-Andes confirmed that the volcanic events affected these areas (Chaperon et al., 2006; Daga et al., 2010, 2012 and its references).

On June 4, 2011, the PCCVC began an eruptive process that generated a column of gases and volcanic ash of >15 km high and 5 km wide reaching the Atlantic Ocean (SERNAGEOMIN/OVDAS, 2011). The plume drifted around the Southern hemisphere reaching Australia in a week. The explosive activity was declining to mixed gas- and ash-jetting since June 2011 to January 2012 (Alloway et al., 2015). The eruption dispersed volcanic products towards the southeast due to meteorological conditions, impacting mainly on the Nahuel Huapi National Park (NHNP; 41° 43' S, 71° 00' W) and the Patagonian Steppe. Previous researches about the volcanic input as a potential source of contaminants in the lacustrine systems were made in the NHNP, North Patagonia, Argentina (Bubach et al., 2012, 2014). Furthermore, volcanic events in the past were considered by Ribeiro Guevara et al. (2010) as an important source of Hg in these areas and even since preindustrial times. This work presents the characterization of changes of the freshwater bodies due to the PCCVC ashes in the NHNP. The main goal was to evaluate the water chemical parameters according to a spatial and temporal distribution. The environmental impact was explored by means of statistic analysis and Pollution Load Index (PLI). The samplings were conducted in two ultra-oligotrophic lakes: Nahuel Huapi and Moreno, located at 30 km and 73 km, respectively, from the volcano source (Fig. 1).

Material and methods

Study area and sampling

The PCCVC includes various fissure vents with aligned domes and pyroclastic cones, with abundance of silicic magma types, unique among the mostly bimodal centers along the SVZ, where basalts widely predominate over more silica-rich rocks (Lara et al., 2006). The latest eruptions from PCCVC produced a dispersion plume which generated a thick white pumice deposit, at 30–40 km from the source; the pyroclastic products were

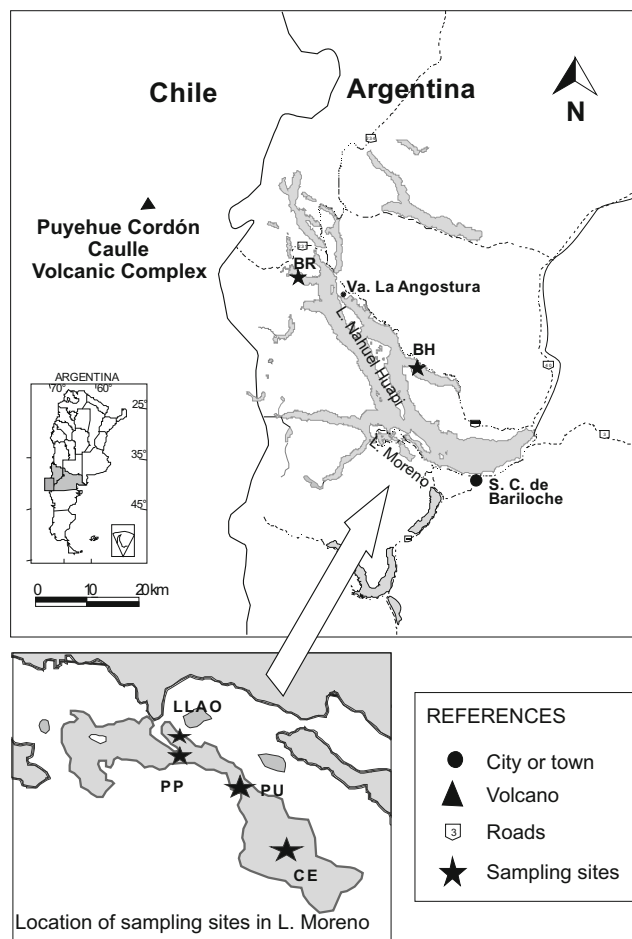


Fig. 1 Location of the Puyehue-Cordón Caulle Volcanic Complex, North Patagonia Argentina. Sampling sites of Lake Nahuel Huapi (BR; BH) and Lake Moreno (LLAO, PP, PU, and CE)

transported to the Argentinean side similar to that of the 1960 event (Petit-Breuilh Sepúlveda, 2004; Lara et al., 2006; Daga et al., 2010; Schipper et al., 2013). The weather in the region is cold temperate continental; the orographic effect of the Andes and the predominant westerly winds determined the moisture which declines from west to east. Mean annual rainfall decreases eastwards more than 3000 mm next to the Chilean Andes, to less than 700 mm at 70 km towards the west. These characteristics were important in relation to the element dispersion plume (Bubach et al., 2012 and 2014). The impacted region by the dispersion of ejected pyroclastic materials during this period was estimated from satellite images (<http://www.nasa.gov/topics/earth/features/20110606-volcano.html>). The lakes chosen for this study were Nahuel Huapi, the largest of the park (total area 557 km² and 464 m depth), and Moreno (10.3 km² total area), a system divided by a close connection into two parts, Moreno West (90 m depth) and Moreno East (maximum depth 112 m). Six sampling sites were selected at different distances from the volcanic source which are listed in Table 1 and showed in Fig. 1. The closest zones to the volcano were Rincón Branch (BR) and Huemul Branch (BH), both in Lake Nahuel Huapi,

Table 1 Sampling sites and geographic coordinates

Lake sampling	Sampling sites	Distance to the volcano (km)	Geographic coordinates	
Nahuel Huapi Lake; Rincón Branch	BR	32.86	40°42'34"S	71°46'56"W
Nahuel Huapi Lake, Huemúl Branch	BH	61.08	40°56'17"S	71°24'30"W
Moreno Lake; West Branch	LLAO	72.21	41°03'717"S	71°325'10"W
	PP	72.93	41°04'22"S	71°31'612"W
Moreno Lake; East Branch	PU*	74.51	41° 04'308"S	71°30'309"W
	CE	78.03	41°06'215"S	71°29'80"W

*The site where the West branch joins with the East branch

and the other four sampling sites in Lake Moreno: Llao Llao (LLAO), panoramic point (PP), the connection of the two branches (PU), and center of the east branch (CE).

The water sample collection was performed after the eruption of PCCVC every 3 months since September 2011 to June 2012. The sampling campaigns were indicated as consecutive numbers as follows: S-1 for springtime 2011, S-2 and S3 correspond to two campaigns in summer 2012, and S-4 for the last sampling in autumn 2012. Table 2 shows the parameters of Lake Nahuel Huapi and Lake Moreno, respectively, which were used as baseline and control samples. The water parameters were taken from published data and/or our previous sampling to the 2011 PCCVC eruption (unpublished data).

Table 2 Average and standard deviations of limnological parameters in WC of lakes Nahuel Huapi and Moreno before the PCCVC event calculated from bibliographic data

	Lake Nahuel Huapi ^a	Lake Moreno ^b
pH (25 °C)	7.2 ± 0.4	7.0 ± 0.4
Cond (µs/cm)	34.1 ± 4.8	36.9 ± 2.3
Na (mg L ⁻¹)	1.7 ± 0.1	1.33 ± 0.09
K (mg L ⁻¹)	0.49 ± 0.01	0.45 ± 0.02
Ca (mg L ⁻¹)	3.1 ± 0.2	4.79 ± 0.01
DIN* (mg L ⁻¹)	9.8 ± 0.1	13.4 ± 0.4
SO ₄ ⁻² (mg L ⁻¹)	1.2 ± 0.1	1.3 ± 0.1
HCO ₃ (mg L ⁻¹)	19 ± 2	23 ± 3
SiO ₂ (mg L ⁻¹)	15 ± 1	10 ± 1
Chl-α (µg L ⁻¹)	1.4 ± 0.3	0.40 ± 0.05
Secchi disc (m)	18 ± -6	15 ± 4
Temp (°C)	10 ± 4	11 ± 5
Eh (mV)	NR	307.6 ± 68.0
THg (ng L ⁻¹)	NR	15 ± 1.4

NR not recorded

*The sum of nitrate, nitrite, and ammonium

^a Diaz et al., 2007; Markert et al., 1997, Donald P. Morris et al., 1995; Pedrozo, et al. 1993

^b Diaz et al. 2007; Donald P. Morris et al., 1995; Queimaliños et al., 1999, Perez et al., 2002 ; our unpublished data

Sampling conditioning and analysis

The samples were collected and stabilized in the field, with suitable reagents according to the requirements, and kept refrigerated until the analysis.

The parameters measured in situ were as follows: depth (eco-sounder Navman Fish 4150), temperature, dissolved oxygen (sensitive electrode HACH Oximeter, Sension 6), and water transparency by Secchi disc.

Water column (WC) samples were taken using a Van Dorm bottle between 20 and 30 m depth and pore water (PW) samples were obtained from sediment water interfaces which were collected by a gravity-activated sediment corer. In the laboratory, the collected material for the PW analysis was centrifuged at 3000 rpm, separated and filtrated. All water samples, procedures, and measurements as pH, Eh, and Cond (pH ion and conductimeter OAKTON) were made following the standard methods for natural water and wastewater analysis (Franson, 1997).

The sample preparation was carried out in a laminar flow hood in order to avoid the pollution. Elemental analysis was performed by atomic absorption spectrometry (AAS) (AAnalyst 300, Perkin Elmer) and selective ion electrode (UV Genesys 20, Thermo Spectronic). Total mercury (THg) was detected by cold vapor atomic fluorescence spectrometry using a pre-oxidation/reduction and amalgamation process (PSA Analytical mod Millennium Merlin System 9) and sulfate analysis (SO₄) by turbidimetric method according ASTM D516-90. The quality of the measurements was tested by Certified Reference Materials (National Research Council Canada, NRC-CNRC ORMS-4). The analyses of the standard reference materials showed good agreement with certified and informed values, and replicate samples were consistent.

Data analysis

The statistical analysis was performed with XL-STAT program, copyright 1995–2009 Addinsoft. The data were

analyzed using a multivariate statistical method (principal component analysis (PCA)). The significance level considered in all statistical tests was $\alpha \leq 0.05$. The quantification of pollution degree in the water was performed using the Tomlinson index, PLI (Tomlinson et al., 1980). This index is based on values of concentration factors (CF) for each element. The CF is the ratio between the elemental concentration in water (Celement) and baseline or background (unpolluted concentration, Cbackground). In this work, background was estimated as mean concentrations from Table 2. For each sampling site, the PLI was calculated as the *n*th root of the product of the *n* CF_{*n*}; (*n* = number of elements).

$$PLI = \sqrt[n]{\prod_1^n CF_n}$$

PLI equal to 1 indicates element loads close to the background level and values above 1 indicate pollution. This empirical index provides a simple way of comparisons among element levels from volcanic inputs. The dissolution index (DI) represents the dissolution process because it was obtained dividing WC by PW concentrations. The DI values were interpreted as suggested by Hakanson (1980) and other authors (Angulo, 1996; Cabrera et al., 1999) where DI < 1 indicates low pollution; 1 < DI < 3 is moderate pollution; 3 < DI < 6 is considerable pollution; and DI > 6 is very high pollution.

Results

Chemical parameters

The datasets of WC and PW by sampling site are presented in Table 3 (ranges, mean, and standard deviation values). Overall, the variables measured in PW were higher than those in WC (see Table 3).

The range of the ash thickness in the studio area was 2.5–22.5 cm being thicker in BR, the site is closer to the volcano source, and the thinner layers corresponded to sites more away from PCCVC as LLAO and PP (Table 3). The Secchi disc data showed a high reduction of transparency for Lake Nahuel Huapi but not in Lake Moreno with respect to the values before the event (Table 2).

The pH range measured was 5.1 to 8.1 (Table 3), and an extreme value (3.2) was found in the CE site in S-4, which was an isolated case. The reported pH of WC in lakes Nahuel Huapi and Moreno before the event were neutral (7.2 ± 0.4 and 7.0 ± 0.4; Table 2), while after PCCVC eruption they reached basic values up to 8.1. Specific conductivity (Cond; Table 3) in WC (28.9–280 µs/cm) is lower than that in PW (30–457 µs/cm), but it always was greater than that before the volcanic event (31.8–39.3 µs/cm; Table 2).

Table 3 Range of variables of WC and PW taken from September 2011 to June 2012, mean and standard deviation (SD)

Sampling site	Thicker ash* cm	Secchi disc m	pH 25 °C	TDS mg L ⁻¹	Cond. µs cm ⁻¹	Eh mV	SO4 mg L ⁻¹	Na mg L ⁻¹	K mg L ⁻¹	Ca mg L ⁻¹	Zn mg L ⁻¹	Al µg L ⁻¹	Cl ⁻ mg L ⁻¹	F ⁻ mg L ⁻¹	THg ng L ⁻¹
BR-WC	23	3–5	5.5–7.3	15.9–27.9	31.8–55.9	369–564	0.7–5.1	2.2–3.2	0.3–0.6	2.2–2.9	0.01–0.6	3.5–4.0	1.25–33.1	0.03–0.08	0.7–9.4
BH-WC	9	6–14	5.1–7.5	14.4–19.2	28.9–39.7	265–562	0.5–2.5	1.6–2.9	0.3–2.0	2.2–3.4	0.01–0.5	1.0–8.9	0.5–3.2	0.02–0.08	2.0–12.0
LLAO-WC	3	9–14	6.8–7.5	18.0–23.3	36.1–46.7	412–545	1.1–2.1	1.2–2.7	0.2–0.5	3.5–5.1	0.01–0.5	0.03–3.75	0.5–122.4	0.02–0.06	1.4–17.3
PP-WC	3	9–14	6.7–7.5	17.9–19.6	35.9–39.2	220–528	1.4–2.1	1.3–2.6	0.2–0.5	3.0–4.4	0.01–0.5	1.0–6.2	0.5–97.4	0.02–0.50	1.2–38.2
PU-WC	3	5–10	5.5–7.4	16.0–23.5	32.1–47.1	204–560	1.6–3.0	1.1–2.3	0.5–0.3	2.3–4.0	0.01–0.5	1.0–13.5	0.5–2.6	0.02–0.05	0.7–27.5
CE-WC	3	9–14	3.2–7.4	16.9–139.0	33.9–280	460–591	1.1–2.7	1.1–2.4	0.2–0.5	2.0–3.8	0.01–0.5	1.0–2.5	0.5–5.7	0.02–0.6	0.5–18.3
Mean ± SD			6.45 ± 1.35	29.3 ± 34.8	58.9 ± 70.0	440 ± 144	2.0 ± 1.3	2.05 ± 0.76	0.51 ± 0.49	3.2 ± 0.9	0.26 ± 0.27	6.9 ± 11.2	22.4 ± 42.2	0.13 ± 0.20	10.8 ± 12.4
BR-PW	23	NR	6.1–7.8	16.3–114.0	32.6–232	194–498	1.7–23.8	1.9–18.5	0.5–2.6	1.3–25.1	0.05–0.7	0.01–280	3.7–14.1	0.09–0.75	<0.5–22.6
BH-PW	9	NR	6.6–7.8	15.0–80.5	30–145.1	171–560	0.2–8.4	1.9–14.4	0.5–2.7	1.9–8.4	0.05–0.9	1.5–11.1	0.5–5.2	0.03–1.1	0.7–10.2
LLAO-PW	3.0	NR	6.7–7.5	30.1–47.1	60.7–95.2	451–560	1.8–6.8	6.4–10.5	0.6–1.3	2.2–6.8	0.1–1.6	2.1–4.75	2.4–8.2	0.1–0.6	0.8–10.2
PP-PW	3.0	NR	6.1–7.5	48.3–90.0	96.5–181	309–509	3.6–21.8	8.4–12.6	0.7–1.2	3.3–5.7	0.2–2.6	2.5–196.9	3.3–14.8	0.04–0.9	0.5–7.6
PU-PW	3.0	NR	7.3–8.1	57.3–228.0	114.6–457	172–570	21.0–48.6	5.5–21.7	0.6–2.5	10.4–68.2	0.05–3.3	1.0–420	3.3–26.6	0.02–0.7	0.7–29.9
CE-PW	3.0	NR	6.2–8.1	56.5–141.0	111.8–3.4	177–432	0.3–11.0	11.0–16.6	0.8–3.2	2.6–18.4	0.2–1.5	0.6–646	3.7–6.7	0.04–0.7	<0.5–14.3
Mean ± SD			7.2 ± 0.8	77.0 ± 60.8	155.0 ± 124.4	383 ± 167	12.4 ± 14.3	10.8 ± 6.3	1.4 ± 1.0	12.9 ± 18.9	0.9 ± 1.1	403.4 ± 602.8	7.6 ± 7.5	0.42 ± 0.40	8.2 ± 9.9

Values in bold show differences with data previous of the PCCVC impact

NR not recorded

*Thicker ash in solid

The Eh for the WC and PW samples post-PCCVC eruption were 440 ± 144 mV and 383 ± 167 mV, respectively. Those values were in the same range with surface ocean water (+400 and +435 mV, pH 7.6–8.3; Wetzel 1983), and also, they were higher than that before the volcano eruption (307 ± 68 mV; Table 2).

The element concentrations in PW were at least twice higher with respect to the WC samples, and the values in the BR, PU, and PP sites were generally the highest. Furthermore, Na, K, and Ca increased in a factor greater than 2 in BR and BH in PW (Tables 2 and 3). A wide range of concentrations in WC for SO₄, Na, K, and Ca (CV 40–96 %) were found; this range included values before the eruption.

Zinc, Al, Cl, and F concentrations presented, also, a great dispersion. The maximum of Zn and Al in PW were 5 to 20 times higher than those in WC, with a maximum in PP and CE sites. Chlorine showed the highest values in WC for the LLAO and PP sites, while F was higher in PW especially for the BH and PP sites.

Total Hg in WC of Lake Moreno before eruption was within the post-eruption range, but the highest concentration in PP (38.2 ng/L) was two times more than that before the event. The PW samples were 25 % lower than those of WC, and the PP site showed also the highest values. In the case of Lake Nahuel Huapi, the THg values were lower than those of Lake Moreno, even before the eruption (Tables 2 and 3).

Pb, Ag, Cr, and As concentrations are shown in Table 4, only when these elements were above to the limit of quantification (LOQ $0.5 \mu\text{g L}^{-1}$). Trace elements were detected and measured in WC at the first sampling; in the subsequent ones, Cr, Pb, and As were only found in PW (Table 4). Arsenic and lead showed similar behavior in PW for sites away from the volcano. The Ag content in Lake Moreno was higher than that in Lake Nahuel Huapi which was more frequently detected in WC. All element concentrations were below the recommended limit for human consumption (ANMAT, 2010).

DI and PLI index

The comparison of DI and PLI in different sites is presented in Table 5 and in Fig. 2. Significant DI were found for Hg and Al. Mercury DI were ≥ 1 ; in particular, the highest were in PP (DI 92) and PU (DI 29) for the first sampling and Al in BR (DI 414) in the last sampling.

Figure 2 shows the PLI tendency to decline with thickness of deposited ash, but it was not correlated significantly. The sampling sites were clearly distinguished by lake, and these are according to the volcano distance. The moderated pollution sites indicated for BR (PLI 2) and BH (PLI 3) of Lake Nahuel Huapi and PP (PLI 2) were very low in LLAO, PU, and CE (PLI < 1) of lake Moreno.

PCA analysis

The PCA ordination diagrams for the WC and PW samples are shown in Figs. 3 and 4, respectively. The principal components (PC1, PC2, and PC3) explained more than 50 % of the total variance. The data for Pb, Ag, Cr, and As were not considered for the PCA, because a few values were only above to the LOQ.

In Fig. 3a, the sampling campaigns S-2 and S-3 were separated from S-1 and S-4 by parameters associated to ash-water interaction such as Secchi, pH, and elements. In Fig. 3b, the highly impacted regions were grouped by a dotted line.

Figure 4a shows the splits of S-2 and S-4 by ash thickness; S-3 by pH, SO₄, and elements like Ca, Cl, and Hg; and S-1 by Zn, F, and Cr. In this case, S-1 was separated from S-2 and S-3, whereas S-4 was next to S-1. In Fig. 4b, all the sampling sites corresponding to S-1 are followed by the S-4 sampling and are enclosed by a dotted black line; next to these, the S-2 which are overlapped with the S-3 sampling sites are delimited by a gray line. Significant correlations among ash thickness, TDS/Cond, and concentrations of some elements in water were obtained and are showed in supplementary data (Table A). Three elements showed temporal correlation, i.e., Cl in S-1 ($r^2 = 0.647$) and S-4 ($r^2 = 0.618$), Hg in S-2 ($r^2 = 0.634$), and Al in S-4 ($r = 0.617$).

Discussion

Oskarsson (1980) argues that the condensation/sublimation of volcanic gases on ash occurs within an eruption plume. Also, the element concentrations in freshly fallen ash are important to assess the plume gas composition and the environmental risk. Same compounds will also adsorb onto ash particles according to relative proportions of HCl, HF, and SO₄ and a number of factors that include the magma type, eruption style, plume temperature, ash load, and particle distribution sizes. The finest particle sizes experiment the highest adsorption that involve high hazard leaching, even if the fallen ash is scarce (Rose et al., 1973; Oskarsson, 1980; Rubin et al., 1994; Witham et al., 2005). However, the chemical risk declines sharply in freshwater 1 day after the ash income, according to Flaathena and Gislason (2007). The volcanic ash entrances to the water body produce a complex chemical process dynamics. The normal water condition can be rapidly reached; nevertheless, it may enclose some environmental risk on bottom sediments.

The Cond is a good approximation of the total dissolved solids (TDS) and the ionic components in solution. The Cond of the hypersaline water (salinity >5 %) is affected by the specific ion compositions, but the correlation with TDS is given only in freshwater bodies and brackish water. Then, this correlation allows to distinguish the “hypersaline” environments from the others (Wetzel 1983). The Cond and TDS

Table 4 Trace element contents in water column (WC) and pore water (PW) of the sampling sites in spring 2011 (S-1), summer 2012 (S-2 and S-3), and autumn 2012 (S-4)

Concentration element (µg/L)	Sampling	Sampling sites						
		BR	BH	LLAO	PA	PU	CE	
Ag	S-1	PW	ND	D		ND	2,2	0,9
		WC	1.5 ± 0.3	0.9 ± 0.2	D	0.6 ± 0.12	0.8 ± 0.2	1.2 ± 0.3
Cr		PW	0.51 ± 0.02	0.73 ± 0.14	1.1 ± 0.22	1.32 ± 0.21	1.32 ± 0.38	2.03 ± 0.41
		WC	0.52 ± 0.02	D	0.63 ± 0.13	D		
Pb		PW	ND					
		WC						
As		PW	ND		6.4 ± 1.3	26.9 ± 4.7	13.3 ± 2.1	7.6 ± 0.2
		WC	D					
Ag	S-2	PW	ND					
		WC	ND					
Cr		PW	D			1.7	1.2	D
		WC	ND					
Pb		PW	ND			5.3 ± 0.9	2.5 ± 0.4	ND
		WC	ND					
As		PW	3.0 ± 0.2	1.2 ± 0.12	3.0 ± 0.5	17.94 ± 3.57	19.16 ± 3.02	1.2 ± 0.2
		WC	ND					
Ag	S-3	PW	ND					
		WC	ND	ND	ND	2.9 ± 0.4	1.2 ± 0.4	1.9 ± 0.6
Cr		PW	ND					
		WC						
Pb		PW	ND	2.5 ± 0.6	50 ± 9	2.5 ± 0.4	12.9 ± 2.1	ND
		WC	ND					0.18 ± 0.05
As		PW	ND					
		WC	ND					
Ag	S-4	PW	ND					
		WC	0.22 ± 0.03	D				0.18
Cr		PW	0.52	2.06	2.06	2.07	0.86	1.44
		WC	D					
Pb		PW	ND	14.34 ± 2.75	10.22 ± 2.03	9.41 ± 0.82	3.55 ± 0.76	3.31 ± 0.62
		WC	ND					
As		PW	ND			14 ± 2	29.0 ± 5.6	10 ± 0.2
		WC	ND					

LOQ limit of quantification (LOQ 0.5 µg L⁻¹), D detected <LOQ, ND not detected <LOQ

could represent an amount of released ions from the ash particle surfaces like SO₄, Cl, Ca, and Na. The quantity of these elements and others like K, Mg, Sr, Li, and U, transported by groundwater in an Etna aquifer, was responsible for the TDS averages (Aiuppa et al., 2000). Our results showed a significant correlation between Cond and TDS (Spearman, *r* = 0.998; Fig. 4a) and changes in the water hardness which was characterized as brackish water after the ash-water interaction (Table 3). Similar behaviors were reported in leaching experiments with volcanic ash, in particular for the Chaitén and Eyjafjallajökull events (Ruggieri et al., 2012; Wall-Palmer et al., 2011; Horwell et al., 2010).

The highest pH and major alkali element concentrations, e.g., Ca and K, were found for S-2 and S-3 sampling (Fig. 4a), and S-4 sampling comes back at the initial state (S-1). These pH changes due to a rapid and great dissolution of alkaline compounds and also the release of hydroxyl ions present on the ash particle surfaces were observed by several authors in other volcanic events (Oelkers and Gislason, 2001; Frogner et al., 2006; Oskarsson, 2009).

Information about low mineralization and unsaturation degree, by means of contact time experiments, showed more effective weathering process when the leaching time was longer (Aiuppa et al., 2000; Ruggieri et al., 2011; Dongarrà et al.,

Table 5 Dissolution index of the different samplings

Sampling			Dissolution index									
Site		Period	SO ₄	Na	K	Ca	Zn	Al	Cl	F	Hg	
Lake Nahuel Huapi	BR	S-1	3	<1	1	1	1	2	<1	<1	<1	
		S-2	<1	<1	<1	<1	1	<1	<1	<1	<1	
		S-3	<1	<1	<1	<1	<1	<1	<1	<1	<1	
		S-4	1	1	1	2	<1	414	9	<1	3	
	BH	S-1	1	1	1	1	1	<1	1	<1	2	
		S-2	1	1	4	1	1	1	1	1	1	
		S-3	<1	<1	<1	<1	<1	<1	<1	<1	<1	
		S-4	6	<1	<1	<1	<1	<1	1	<1	3	
Lake Moreno	LLAO	S-1	1	<1	<1	1	<1	<1	<1	<1	2	
		S-2	<1	<1	1	1	<1	<1	16	<1	1	
		S-3	<1	<1	<1	1	<1	<1	<1	<1	<1	
		S-4	1	<1	<1	2	<1	<1	<1	<1	2	
	PP	S-1	<1	<1	<1	1	<1	<1	<1	1	92	
		S-2	<1	<1	1	1	<1	<1	7	<1	<1	
		S-3	<1	<1	<1	1	<1	<1	<1	<1	6	
		S-4	<1	<1	<1	1	<1	1	1	1	1	
	PU	S-1	<1	<1	<1	<1	<1	<1	<1	<1	29	
		S-2	<1	<1	<1	<1	1	<1	<1	<1	1	
		S-3	<1	<1	<1	<1	<1	<1	<1	<1	1	
		S-4	<1	<1	1	<1	<1	1	1	1	1	
	CE	S-1	<1	<1	<1	1	<1	<1	<1	1	2	
		S-2	<1	<1	<1	<1	<1	<1	1	<1	2	
		S-3	2	<1	<1	<1	<1	<1	<1	<1	1	
		S-4	11	<1	<1	1	<1	2	1	1	2	

DI > 1 indicates that concentration in WC increased from PW

2009). This could explain the relation between PW and WC in our results (Table 3). The ranges of TDS, pH, and ionic composition in the PW samples were significantly greater than those in the WC ones. The pH range in PW was 6.1 to 8.1 and TDS from 15 to 228 mg/L dominated by Al, Ca, Na, and SO₄ (Table 3). While WC had low salinity ($15.9 < \text{TDS} < 139 \text{ mg/L}$; Table 3) and its pH range was 5.1–7.5, only one sample had extreme data (pH 3.2 and TDS > 139 mg/L). Furthermore, the increase in Eh after the ash

fall indicated chemical changes in WC ($440 \pm 144 \text{ mV}$) and probably too in PW ($383 \pm 167 \text{ mV}$; Table 3).

Ruggieri et al. (2012) demonstrated that the main environmental impact from volcano ashes was by incorporations of elements like As, Cr, Fe, Ca, and Zn. These elements and K were also released from Chaitén ash during the initial exposure, where at least 20 % of dissolved total Ca was assigned to this (Martin et al., 2009; Ruggieri et al., 2011, 2012; Durant et al., 2012). In our study, the Ca content in WC ($3.2 \pm 0.9 \text{ mg/L}$) was in the order of previous data to the event and with a great dispersion (3.1 ± 0.2 to $4.79 \pm 0.01 \text{ mg/L}$ in Table 2). The Ca content could be associated with watering process and gas dissolution.

Measured Cr in both PW and WC samples of the first and fourth sampling (Table 4) were in agreement to the PCCVC studies about the variation of plume composition published by Daga et al. (2014) and its association with the particulate matter observed in lichens (Bubach et al., 2012). Therefore, the incorporation of compounds and gas from PCCVC ashes affected the solubilization and precipitation process in the water column. The changes among pH, Cond, TDS, Secchi disc, and Eh before, during, and after the event could have affected the optimal life conditions for the organisms (Tables 2 to 4 and

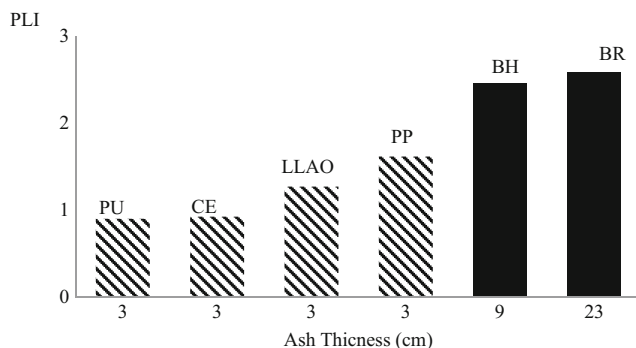


Fig. 2 Pollution Load Index (PLI) of sampling sites. *Black pattern* indicates Lake Nahuel Huapi and Moreno in *stripes*. The PLI = 1 indicates load of elements close to the background level, and values above 1 indicate pollution

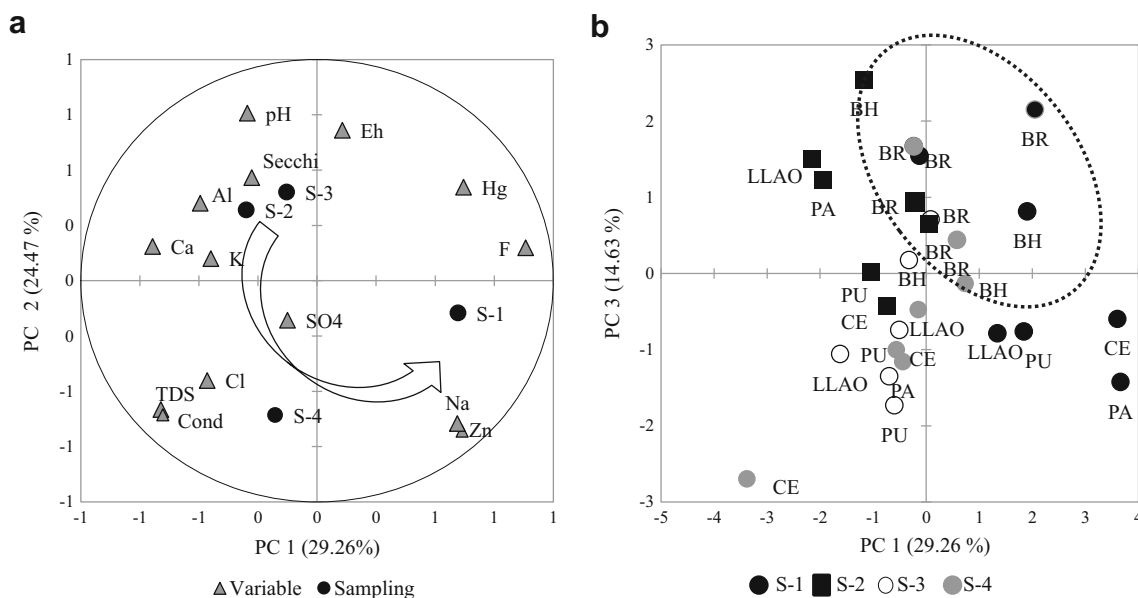


Fig. 3 Biplot PCA of WC. **a** The *points* represent the sampling sites in different seasons, springtime 2011 (S-1), summer 2012 (S-2 and S-3), and autumn 2012 (S-4). The *triangles* represent each variable. **b** The sampling sites in the different seasons

Figs. 3a and 4a). These were associated with lake transparency and low TDS like indicated by Woliński et al. (2013) for *Cladocera* populations.

On the other hand, the evaluation of environmental volcano impact at long term by leaching tests demonstrated that the significant load of pollutants was released from the particle surface at different times. For example, As, Cr, and Fe escaped during the initial exposure, while other elements require lower rates for weathering processes and glass dissolving (Martin et al., 2009; Ruggieri et al., 2011, 2012; Durant et al., 2012).

These different leaching rates could explain our results, particularly for Cr in S-4 as shown in Table 4.

Fluoride is a typical element after tephra fall and can be mainly enriched with respect to the original magmatic content, in a factor of six (Martin et al., 2012; Straub and Layne, 2003; Witham et al., 2005). Several researches on F release experiments indicated the freeing dependency with their chemical form (Cronin et al., 2003; Christenson, 2000; Oskarsson, 1980). Cronin and Sharp (2002) showed an underestimation of F-risk after fallen tephra. Fluoride in our study was lower in

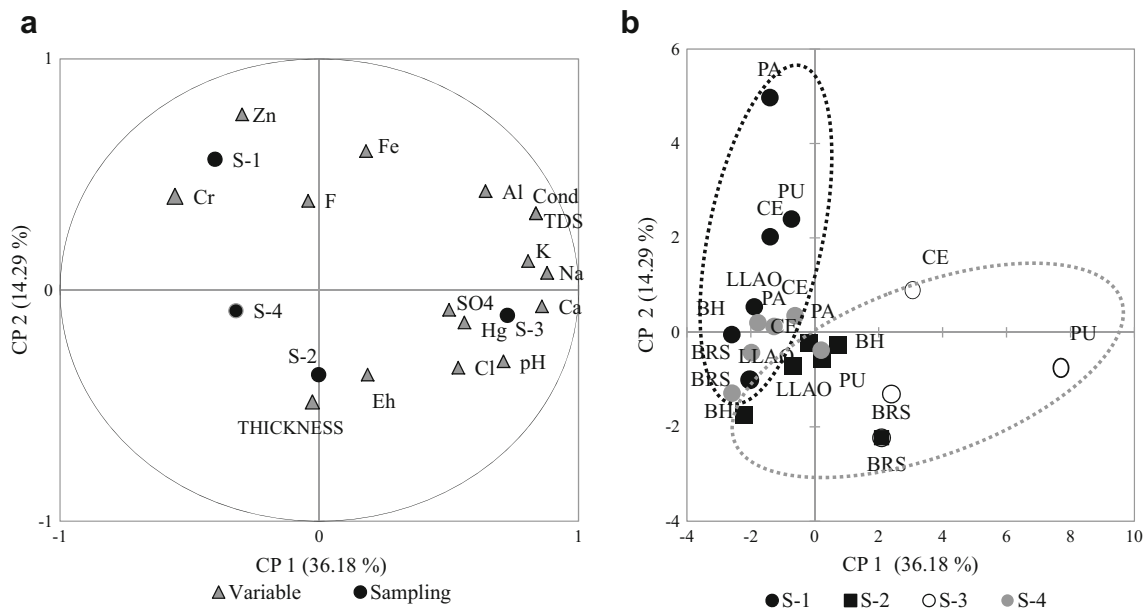


Fig. 4 Biplot PCA of PW. **a** The *points* represent the sampling sites in different seasons, springtime 2011 (S-1), summer 2012 (S-2 and S-3), and autumn 2012 (S-4). The *triangles* represent each variable. **b** The sampling sites in the different seasons

WC than in PW for all sites (Table 3), and this could be a potential hazard for the environment at long term.

The mobile elements associated to the particle surfaces were discriminated according to DI values from other elements with most complex and strong bond. The PLI allowed to evaluate each site considering all elements. The located sites further away from the PCCVC in Lake Moreno (LLAO, PP, PU, and CE) showed low modification by the ash fall according to its DI and PLI indices. The BR and BH sites in Lake Nahuel Huapi, which were closer to the source, indicated moderated impact ($DI > 1$ and $PLI > 2$). These agree with the PCA analysis, where the sites were grouped according to PCCVC distance (Fig. 3b) and the sampling sequence (Figs. 3a and 4b); the parameters like SO_4 , Na, and Zn determined the proximity of point S-1 and S-4 in both Figs. 3a and 4a. These results agree with impacts without mudflow and neither big ash deposits and where the chemical composition showed little modifications, i.e., Lakes Amber, Sprague, and Warden by the Mount St. Helens eruption in 1980 (Lee, 1996). This effect should be considered as a dynamic equilibrium of the interaction between water and ash.

Mt. Etna was clearly identified as the major source of volcanic Hg, and it represents the principal deposition source in the Mediterranean region (Martin et al., 2011, 2012). There are considerable agreement regarding to the Hg volcanic impact at a local scale, but there is uncertainty in our region (Schroeder and Munthe, 1998). Mercury inputs on the lake sediment profile of NHNP were linked to past volcanic events by Ribeiro Guevara et al. (2010). Furthermore, bioindication studies of volatile element emissions by PCCVC showed that the Hg content in lichens could not be linked to this event (Bubach et al. 2014). Total Hg is highly correlated with total suspended sediment concentrations due to sedimentation patterns, which is strongly influenced by fine particles and dissolved organic carbon (Roulet et al., 1998; Balogh et al. 1996; Bravo et al. 2011). According to these, THg levels in PU and CE with respect to PP (Table 3) could be explained by differences of transport and deposition of associated sediments with water stream. The water flows from CE in Moreno East through the PU site connecting to Moreno West and reaching up to PP which is the deepest area of Moreno (Fig. 1). On the other hand, the PLI value in the PP site was the highest, due to Hg concentration in water with respect to the background which was 128 and its DI is 92, which were approximately double or more than in the other sites (Fig. 2 and Table 5).

Summarizing

The determined elemental concentrations and physicochemical parameters in water samples allowed to identify changes by deposited volcanic ashes throughout 1 year of eruption. The lake parameters showed the tendency to recover the initial

state. The water chemistry data interpretation in the study area indicated that the processes were controlled by a complex interaction between various geochemical processes like adsorption/desorption, leaching, and mixing with freshwater. The impact degree was affected by the volume and ash composition, and these processes began when ashes income to the water. The major changes for PLI were observed in closest locations to PCCVC. These sites had large variation of pH (5.1–8.1), Eh (415.33 ± 127.81 mV), conductivity (28.9–457 $\mu\text{S}/\text{cm}$), and, also, concentration elements like Na, Ca, Al, Cl, F, and SO_4 . Trace elements such as Cr, Hg, and Ag were detected and measured in the WC samples at the first sampling, and in the subsequent ones, only were found Cr, Pb, and As for the PW samples.

The evaluation of Hg impact showed that Hg appears after the event in water column, but it was not clear if the Hg comes from the freshly fallen ash or if the chemical conditions could be able to release the Hg from the bottom sediments due to the ash income; specific experiments would be needed to classify this point.

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