



Iron buffer system in the water column and partitioning in the sediments of the naturally acidic Lake Caviahue, Neuquén, Argentina



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ABSTRACT

Sedimentary iron partitioning was studied for five sediment strata (16 cm depth) at three sampling sites of the naturally-occurring acidic Lake Caviahue (Patagonia, Argentina). Additionally, water column iron was modeled based on five-year period input loadings to study a possible iron buffer system. The partition coefficient between the water column and the total iron content of the sediments was also addressed. Sedimentary iron was found to be distributed, on average, in the following forms: exchangeable (6%), iron oxides (4%), pyrite and reactive organic matter (38%) and residual (non-andesitic) materials with a high content of humic acids (52%). Furthermore, we found that the dissolved iron in the lake was nearly constant throughout the five year period we studied. This is consistent with the existence of an iron buffer system in the lake at pH between 2.0 and 3.0, which may cause differential iron precipitation at the delta of the volcanic river with respect to the deeper northern and southern arms. Sedimentary iron measurements taken at the delta further support the existence of a buffer system, where it was found that the iron content in the sub-superficial stratum (2 cm) was double that of the remainder of the vertical profile at the same site.

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1. Introduction

Strong acids may be introduced into surface waters through at least three pathways: volcanic activity, acidic mine drainage (AMD) and natural weathering of pyrite rich rocks (natural equivalent of AMD). Contributions from acid rain, while present, are negligible compared with the first two. Both natural and anthropogenic sources may lead to strongly acidic lakes and rivers (pH < 4.0). Due to the increase in the solubility of metals at lower pH, very high concentrations can often be found of a wide spectrum of elements such as iron and aluminum (Stumm and Morgan, 1996; Geller et al., 1998).

Hydrochemical, geochemical and limnological effects of acidification have been described most extensively for anthropogenically acidified surface water bodies (Dillon et al., 1984). In recent years much work has been done to better understand waters that are highly acidic naturally due to volcanic activity (Pedrozo et al., 2001; Wendt-Potthoff and Koschorreck, 2002; Marini et al., 2003; Gammons et al., 2005; Beamud et al., 2007; Llames and Vinocur, 2007; Koschorreck et al., 2008; Pedrozo et al., 2008; Varekamp, 2008; Varekamp et al., 2009; Beamud et al., 2010; Chiacchiarini et al., 2010, among many others).

Patagonian lakes and reservoirs span a wide pH gradient. Andean lakes are neutral, deep and ultra-oligotrophic, while those of the Patagonian plateau are alkaline, shallow, eutrophic and hyperhaline (Pedrozo et al., 1993). Lake Caviahue, the subject of the present study, is very

acid, deep oligotrophic with low planktonic diversity and is unique in South America (Pedrozo et al., 2001; Pedrozo et al., 2008). Located deep in the Andean Mountains (Fig. 1), the special characteristics that differentiate it from the other lakes of the region are due primarily to the activity of the Copahue Volcano (Delpino et al., 1997; Diaz et al., 2007; Varekamp, 2008).

Sedimentary iron and trace metals are often found associated to different chemical phases, such as the exchangeable fraction, carbonates, iron and manganese oxides, monosulfides (FeS), pyrite (FeS₂), mineral rocks and in organic matter (OM). In organic matter, iron can be found in tissue or cell walls of living organisms, detritus, soluble humic substances (HS) with low molecular weight as well as in HS coatings on mineral particles (Tessier et al., 1979). The distribution of iron is governed by local physico-chemical conditions such as pH and electric potential, Eh (Butler and Rickard, 2000).

Most geochemical studies of the metal partitioning of sediments in acidic environments have focused on AMD, for example in the Iberian Pyrite Belt, the Mining Lakes District in Germany or massive sulfide deposits in the Yukon Territory, Canada (Geller et al., 1998; Friese et al., 1998; Kwong and Lawrence, 1998; Bachmann et al., 2001; Torres and Auleda, 2013). Investigations of sediments of naturally acidic water bodies have mainly analyzed total metal content and mineralogy rather than partitioning. Several methods have been used to determine total metal content including digestion with strong acids and other oxidant mixtures (HF, HCl, HClO₄, HNO₃, HSO₄, H₂O₂), energy dispersive spectroscopy, total reflexion X-ray fluorescence and X-ray diffraction (Delmelle and Bernard, 1994; McKenzie et al., 2001; Ruiz-Fernández et al., 2007; Ma et al., 2011).

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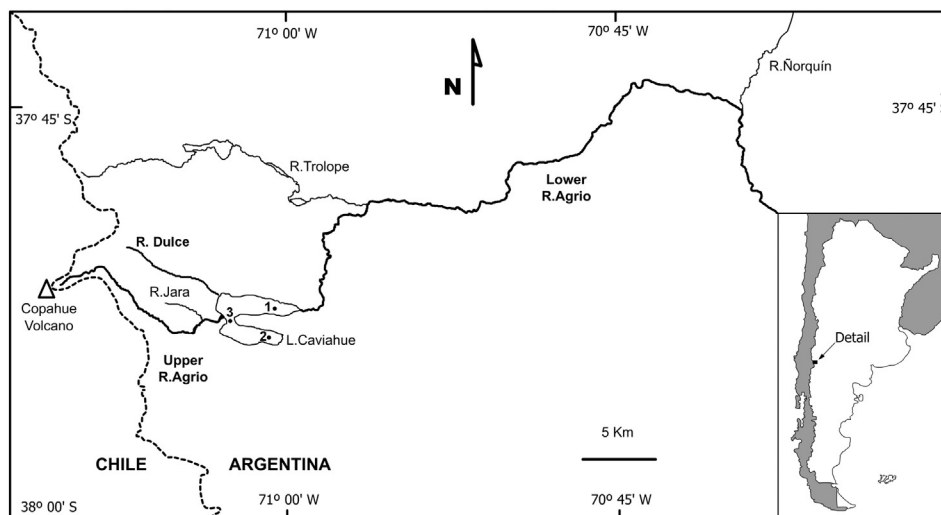


Fig. 1. Study area: Copahue Volcano, Lake Caviahue, URA, Dulce and LRA rivers. Sampling stations were located in the deeper sites of the northern (1) and southern (2) arms, and in the union of both arms at the Agrio River delta, the Center of the lake (3).

Objectives of the present study are to determine and analyze the distribution of iron in the highly acidic sediments of Lake Caviahue, and the relation between this distribution and the iron concentration in the water column.

Our findings will allow for the prediction of new scenarios in iron cycling if, due to volcanic activity, changes occur in the acidity of the lake or redox conditions (Eggleton and Thomas, 2004).

2. Study area

Lake Caviahue is located 1600 m.a.s.l. in the Copahue-Caviahue Provincial Park (37° 53' S; 71° 02' W), Neuquén, Argentina (Fig. 1). The lake is a naturally-occurring glaciated water body with a maximum length of 9.7 km, maximum width of 4.7 km, coastline of 22.3 km, total area of 9.2 km² and total volume of 0.47 km³. The water residence time (*R*) has been estimated by two authors in two different ways: Rapacioli (1985) estimated 31.2 months based on hydrological calculations while Varekamp (2003, 2008) predicted 42 months based on conservative element loadings and concentration. It has a horseshoe shape with two arms (northern and southern) 90 m and 70 m deep, respectively, and the two mayor influxes are the Dulce River (average flow of 1.23 m³ s⁻¹) and the Upper Rio Agrio (URA, average flow of 1.10 m³ s⁻¹). The former is a scrubby forested, soil-covered basin with a pH of 6.5, while the latter is born on the east slope of the Copahue Volcano caldera and has an initial pH of 0.8, a temperature of 56 to 82 °C, a conductivity of 560 mS cm⁻¹ (Pedrozo et al., 2001; Pedrozo et al., 2008) and flows into the lake with a pH of 1.9 to 2.5. While both tributaries discharge into the northern arm, the URA joins the lake at a point closer to the union of the arms. Caviahue has a pH of 2.2 to 3.0, high electric conductivity (560 to 1600 μS cm⁻¹) and high concentrations of PO₄³⁻ (210 to 240 μg L⁻¹), Fe (20 mg L⁻¹), Al (27 mg L⁻¹), Mn (1 mg L⁻¹), Cl (95 mg L⁻¹), F (6.7 mg L⁻¹), Si (17 mg L⁻¹), SO₄²⁻ (400 mg L⁻¹), Na (14 mg L⁻¹), K (6 mg L⁻¹), Ca (22 mg L⁻¹) and other trace elements (Pedrozo et al., 2001; Pedrozo et al., 2008; Varekamp, 2008) and this is why Lake Caviahue is unique among Andean lakes, which are usually circumneutral and oligotrophic (Diaz et al., 2007).

The effluent is the Lower Rio Agrio (LRA), which exits the lake with a pH near 3.0 and joins the Neuquén River approximately 200 km downstream with a pH of 8.0 due to the contribution of several dilute tributaries.

The predominant mineral throughout the basin is andesitic (Pesce, 1989; Varekamp et al., 2006) although much of the sediment input since year 2000 is probably ash from the eruption that took place that year (basaltic andesite, Varekamp, 2015). The organic matter content

of the lake sediment is between 5 and 10%, and is rich in phosphorus (1 mg g⁻¹ associated with the organic fraction). The average Eh is -120 mV (-20/-180 mV), and the pH ranges between 3.0 and 4.0 for both basins, and between 3.0 and 6.0 at the union of both arms (Temporetti et al., 2013 and data not published).

Located on the west side of the northern arm is the town of Caviahue. It has approximately 900 permanent inhabitants, although the population varies throughout the year due to incoming tourists that visit the thermal bath complex and the sky resort located on the Copahue Volcano.

3. Materials and methods

3.1. Sample collection, processing and in situ measurements

Sediment cores were collected with a 6 cm diameter, Uwitec-type corer in January of 2013 at three stations: the deepest sites of both arms, northern (NA) and southern (SA), and at the Center (C) (Fig. 1). Each core was sliced into five strata, 2 cm thick in the upper horizon (0 to 4 cm) and 4 cm thereafter (4 to 16 cm). Eh and pH (Orion 920A) measurements, adjusting for temperature, were taken in each stratum. Samples were stored in polyethylene bags in a N₂ atmosphere at 4 °C for no longer than 24 h before being frozen. All analyses were performed within one week.

Concurrently, water samples were collected from the same sites at various depths using a 4 L Van Dorn bottle. Additional samples were taken along a transect extending into the lake from a point 50 m upstream of the URA discharge site. Measurements were made at the start point of the transect located in the river, at the coastline (discharge point) and at a distance of 5, 50, 100 and 250 m into the lake. Samples were filtered (0.45 μm acetate filters) and stored in polyethylene bottles at 4 °C for further metal analysis (water pH 2.0).

In the years 1999 and 2000, water samples were taken for the simulation of the saturation indexes following the same method as Pedrozo et al. (2001). Samples were analyzed as described in Section 3.3.3 at the Helmholtz Centre for Environmental Research in Magdeburg, Germany.

In the laboratory, sediment samples from all strata were carefully homogenized by hand inside a container bag (under a N₂ atmosphere). Aliquots with a dry weight (dw) of 1 g were stored in polypropylene tubes for metal extraction. All analyses were performed on fresh anoxic sediments under anaerobic conditions in order to preserve the metal distribution among the sediment fractions. Reagents were of analytical grade, and MilliQ water was used. Oxygen in the reagents was removed by N₂ bubbling. The extraction procedures were performed within 48 h of sub-sampling.

3.2. Organic matter, water content and humic acid content

Fresh sediment was dried by one of two methods: in an oven at 60 °C for 72 h (constant weight) to estimate water content and in a vacuum desiccator until a constant weight was reached for SEM microscopy.

Total organic matter was taken as the difference between the dry weight and ash weight (muffled at 550 °C for 4 h).

Humic acids (HA) were extracted from dry sediments (dried at 60 °C) following the methodology recommended by the International Humic Substances Society and as done by Swift (1996). After dialysis, the samples were washed three times with a 1 M HCl solution in order to reduce the metal content, then freeze-dried and weighed for yield calculations (Hering and Morel, 1988).

3.3. Chemical analysis

3.3.1. Iron sequential extraction

Sedimentary iron partitioning was analyzed using the sequential extraction (SE) scheme proposed by Tessier et al. (1979) on three replicates. Two modifications were applied to the method. First, the two initial steps were combined and the MgCl step was eliminated based on the absence of carbonates in the sediments (Temporetti et al., 2013) and on prior analyses of the samples performed in our lab (data not shown). Henceforth the extraction treated with NaOAc with a pH of 5.0 will be referred to as exchangeable. The second modification regards the total digestion and was the adoption of the method proposed by Carter (1993), which employs boiling H₂SO₄ and H₂O₂ instead of the more aggressive HClO₄-HF. As organic matter remained in the sediments following the oxidation step (85 °C H₂O₂ for 5 h), with the Carter method the andesite was not destroyed, and the iron associated with the remaining non-mineral material could therefore be quantified. Other authors have similarly found that H₂O₂ oxidation does not completely destroy recalcitrant organic matter (Tessier et al., 1979; Gleyzes et al., 2002; Jin et al., 2008). In addition, clay content was expected to be negligible (Temporetti et al., 2013).

A second iron extraction was performed on three replicates with a 1 M HCl wash as done in Allen et al. (1993), for the purpose of comparison with the SE exchangeable extraction.

Iron was analyzed in both sediment and water samples by air-acetylene flame atomic absorption spectroscopy (FAAS) with deuterium background correction, and quantified with matrix-matched standards. Dilutions were done when necessary. Detection limit was 0.1 mg L⁻¹ of Fe.

3.3.2. Iron concentration in the water column

3.3.2.1. Iron concentration and partition coefficients. Total iron concentration was determined for all water samples in order to estimate the partition coefficient $II = C_{sil}/C_{di}$. C_{si} is the concentration of sedimentary iron and C_{di} is the dissolved iron in the water column (O'Connor, 1988). Iron was quantified according to the procedure described in Section 3.3.1 using MilliQ water as blank.

Table 1

Sampling date (dd/mm/yy), lake pH, Q_{if} : inflow, L_{inf} : Agrio River iron loadings and lake iron concentration. (*): taken from Varekamp (2008).

Sampling date	pH	Q_{if} (m ³ /s)	Fe L_{inf} (tonnes/m)	[Fe] Lake (mg L ⁻¹)
23/03/99	2.11	0.71	530	21.5
19/06/99	N/D	1.84	625	19.6
21/12/99	2.45	2.16	297	20.4
15/01/00	2.30	1.68	231	21.2
19/07/00	2.20	3.30*	1121	20.8
11/11/00	2.61	2.80	138	21.9
04/03/01	2.45	0.67	313	21.4
20/03/03	2.63	0.96	458	23.1
17/03/04	2.76	0.35	283	22.4

3.3.2.2. Modeled iron concentration. Expected iron concentration was modeled for the years in which inputs significantly above the average were registered, using Varekamp's (2003, 2008) for progressive contamination in perfectly mixed lakes. Iron loadings, pH, and lake concentrations for the period between March 1999 and March 2004 were taken from the dataset published by Pedrozo et al. (2008) (Table 2). In this dataset there are three sampling dates for each of the first two years and one per year thereafter.

Varekamp's equation is given by $C_t = C_{ss}(1 - e^{-t/R}) + C_0 e^{-t/R}$, where C_t is the concentration at a given time (t) and influx (L_{inf}), R is the water residence time and C_0 is the initial concentration of each step. The steady state concentration C_{ss} was calculated as $L_{inf} R/V$, where V is the volume of the lake. The water and conservative element residence time used for modeling is 31.2 months (Rapacioli, 1985) because it allowed the best correlation between the observed and predicted data. The nearest neighbor interpolation was used to feed the model with constant influx values. The one exception was for July 2000 (Varekamp, 2008) due to a volcanic eruption, which did not last for the duration of the sample period. The loading values corresponding to this date (Table 1) were held constant for only two months and are the highest on record. Finally, the loadings (L_{in}) and initial concentrations (C_0) were reset together at every step.

3.3.3. Saturation indexes

Saturation indexes for minerals were calculated for NA and SA using Visual MINTEQ 3.0. Concentrations of Ba, Cd, Cu, Cr, and Ni were determined with ICP-MS, As, Br, Cl, Co, Fe, Hg, Mn, Mo, Rb, Sr, Pb, V, and Zn with total reflection X-ray fluorescence (TXRF), Al, Ca, K, Mg, and Na with ICP-OES; NH₄, NO₃, NO₂, SRP, TP, and SO₄ with a SFA nutrient analyzer and DOC with a TOC-IR analyzer.

Saturation indexes were calculated for two periods: pre- and post-eruption (1999 and late 2000). Only the over-saturated minerals are listed.

3.4. SEM and EDS analysis

Sample surface morphology and elemental composition was investigated using a SEM Phillips 515 equipped with an X-ray energy dispersive spectrometer (EDS).

3.5. Statistical analysis

The Kruskal Wallis (KW) test was used to determine significant differences among sites in metal concentrations, pH, Eh, OM and HA. Contrast analysis was used to validate the differences found with the KW test. The significance level was fixed at $\alpha = 0.05$.

The degree of correlation between the studied variables was determined using the Pearson's correlation test.

Infostat 2014 software was used to perform all analyses.

4. Results

4.1. pH and Eh for the sediments

The pH measurements show an increased with sediment depth (pH of 3.0 to 4.0), at a similar rate for both NA and SA. While C follows the same trend, pH (as high as 6.0) increased more at lower depths (Fig. 2.a).

Eh also rose in the downward direction at all three sites. Again the results for the arms were similar, with the exception of the superficial horizon where the value of NA was half that of SA. The measurements on C sediments yielded lower values from 0 to 12 cm but they increased at the deeper stratum (Fig. 2.a).

Eh for the water column above the sediments was +680 mV and average pH = 2.9.

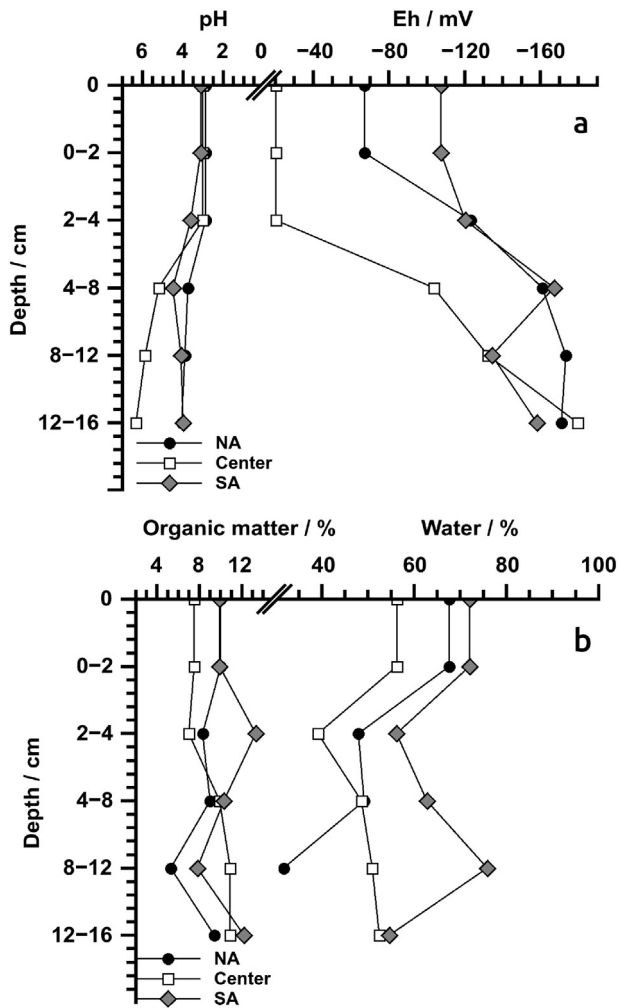


Fig. 2. pH, Eh, OM and water content vertical profiles of the sediments, a: pH and redox potentials, b: organic matter and water content.

4.2. Water, organic matter and humic acid content

Sediment water content patterns were similar for NA and SA (higher values for the SA) and more variable compared with C. At C and NA the average water percentage was about 50% whereas it was about 63% for the SA (Fig. 2.b).

The bottom stratum of NA was more packed and sandy than in any of the other samples processed (water content 30% below average), thus the corer did not penetrate any further.

Sediments contained an average organic matter (OM) content of between 5 and 13%. HA ranged from 0.5 to 3.5% and no relationship was observed with total OM. While total HA at NA dropped by 75% between upper and lower strata (2.2 to 0.5% average content, Fig. 3), total OM fell by only 50% (10 to 5%). OM followed the same trend at SA but with higher values, while HA concentration increased from 2.5 to 3.5% before it finally dropped to 1.5%. Lastly, at C OM rose from 7.5 to 11% as HA dropped from 1 to 0.5%.

4.3. Iron partitioning by sequential extraction

The results of the sequential extraction procedure (Fig. 3) indicate that the iron associated with the exchangeable/carbonates and reducible fractions (F1 and F2) on average accounted for $6 \pm 1\%$ and $4 \pm 1\%$ of the total iron content, respectively. The most enriched iron fractions were the oxidizable (F3) and residual (F4—not andesitic), and these accounted for $38 \pm 10\%$ and $52 \pm 11\%$ of the total, respectively. The results of the HCl extraction were comparable with those of the exchangeable.

In the vertical profile, the F4 fraction accounted for 73 to 0% of the total iron content at the NA, 17 to 70% at C and 40 to 60% at SA, which indicates different patterns for each sampling site. The trends observed in the HA content mirrored those of the arms (Fig. 3).

At NA, the F3 metal fraction increased with depth (opposite of the tendency of F4). At C site, however, the F3 was greatest in the second stratum where it comprised 80% of the total iron concentration, compared to an average of 15% in the other strata. The oxidizable fraction of SA increased between the first and second strata, then reached a minimum before rising again in the fourth and fifth. In summary, exacted fractions all exhibited similar trends at the SA and the Center sites, while at NA different patterns were observed with the exception of total iron.

Total iron concentrations were significantly different among strata ($p < 0.0063$) but a similar tendency can be observed at the 3 sites (Table 2). NA and SA have similar increase and decrease percentages except for the second transition, while the percentages of the Center strata are only comparable to the NA and SA at the second and fourth transitions, respectively.

Strong and significant variations were observed between strata at each site for all variables. Among the three sites a regular pattern emerges (Table 3). When significant differences were present, two clusters were found in the metal extraction data: at NA and SA, and Center. In all of the metal extractions, the mean iron content was higher at the arms than Center. This was not the case for the exchangeable and HCl fractions where differences were not significant.

OM data at SA was comparable to that C, whereas the water percentage at the latter was equal to NA. Regarding HA, the extraction yield was different for all three sites, with the highest concentration at SA and lowest at C (Table 3).

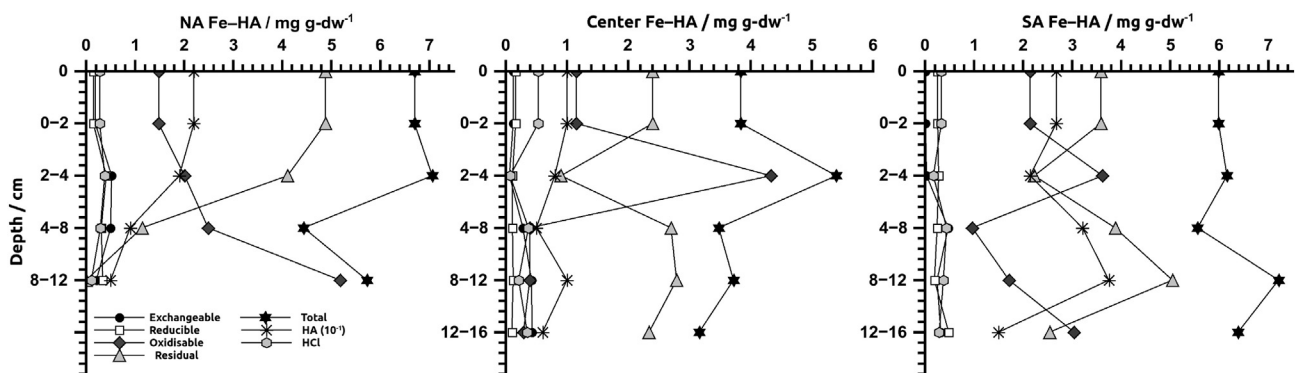


Fig. 3. Sequential extraction (SE) vertical profiles for the NA, C and SA sampling sites. The SE yields are compared to reactive iron and HA sedimentary content (expressed as 10^{-1} to fit the scale).

Table 2

Differences (%) in sedimentary iron between strata. (N/D: not determined). The arrows indicate increase or decrease in total iron content from a certain stratum to the following one.

Stratum transition	NA (%)	Center (%)	SA (%)
0–2 → 2–4	↑ 5.3	↑ 40	↑ 2.9
2–4 → 4–8	↓ 37	↓ 35	↓ 10
4–8 → 8–12	↑ 28	↑ 6.7	↑ 29
8–12 → 12–16	N/D	↓ 15	↓ 11

4.4. Iron concentration in the water column

4.4.1. Iron concentration and partition coefficients

Total iron concentration was not significantly different at the three sites (Table 4). The mean value was $17.1 \pm 0.3 \text{ mg L}^{-1}$. Following the practice of Gammons et al. (2005), differences were considered to be significant if the standard deviation was higher than 5%.

The results along the transect from the coastline into the NA show that iron concentration at the Rio Agrio discharge point was 16% higher than at the lake (5 to 250 m) and 53% lower than the incoming river.

The partition coefficients Π for the three sampling stations were 385, 220 and 321 for NA, C and SA respectively. The values at the northern and southern arms were closer to one another than to the Center.

4.4.2. Modeled concentrations

Lake iron concentration was accurately described by the model described in Section 3.3.2.2 (Fig. 4) after the 16th month, when inputs were close to or below average ($388 \text{ tonnes month}^{-1}$). Larger discrepancies were observed for the first ten months and as well as the 16th due to the influence of above average loadings. The expected steady state concentration (C_{ss}) was 35 to 44 mg L^{-1} for the first four months, and while the modeled concentration increased, the measured lake concentration did not. During the following months iron concentration decreased as a consequence of lower input values. Between the 10th and 16th months, the predicted values were slightly higher than the measured values. Both converge after the 18th month with a mean of 21 mg L^{-1} , which indicates a high degree of correlation ($r = 0.92$; $p = 0.016$) between model data and observations. Although only since the 20th month the observed and predicted values were significantly equal (Kolmogorov–Smirnov, $D = 0.77$; $p > 0.05$).

4.4.3. Saturation indexes

Over-saturated indexes were only registered for iron-based minerals (oxides, oxo-hydroxides and sulfates). As can be seen in Table 5, values after the eruption were slightly higher due probably to a small rise in pH.

4.5. SEM–EDS analysis

As reported by Pesce (1989) and Temporetti et al. (2013), the predominant mineral material in the sediments is andesitic rock. About 0.5% of the sediments consisted of extractable metals, and of this

Table 3

Kruskal–Wallis test results. Significant differences ($p < 0.05$) are expressed with different letters, means values for each group are expressed in mg g-dw^{-1} for iron content and % for HA and MO content.

Variable/site	NA	C	SA	p value	Mean values (mg g-dw^{-1} and %)		
Fe-exchangeable	a	a	a	0.070	a = 0.27		
Fe-reducible	a	b	a	>0.0001	a = 0.28	b = 0.12	
Fe-oxidizable	a	b	a	0.0044	a = 2.46	b = 1.31	
Fe-residual	a	a	a	0.229	a = 2.66		
Fe-total	a	b	a	>0.0001	a = 5.91	b = 3.92	
%HA	a	b	c	0.0001	a = 1.38	b = 0.77	c = 2.49
%MO	a	b	b	0.015	a = 8.13	b = 9.97	

Table 4

January 2013 iron concentrations at the sampling stations (surface and bottom waters).

Sample (m)	Fe [mg L^{-1}]
NA 0	17.4
NA 90	17.4
C 0	16.8
C 20	17.3
SA 0	16.8
SA 65	17.1

fraction 95% was iron. Framboidal pyrite crystals were observed in strata with a higher F3 (oxidizable) content, the composition of which (FeS_2) was determined by EDS. As in previous studies, clay was not detected.

5. Discussion

5.1. Sedimentary iron

The different combinations of pH and Eh values found in the sediments do not favor pyrite formation. Under the conditions we found in Caviahue, according to Butler and Rickard (2000) highly stable pyrite will form when iron (II) is over-saturated at concentrations between 55 mg L-pw^{-1} and $5500 \text{ mg L-pw}^{-1}$. Also unfavorable in these conditions (pH below 5) is the synthesis of metal sulfides and carbonates. As expected, less iron associated with these fractions was measured. Iron or manganese hydroxides were similarly not expected in large amounts due to a pH of less than 3.5 and Eh less than -120 mV (Stumm and Morgan, 1996). Highly organic matter and humic substances can keep iron in complexed form, as dissolved, precipitated or aggregated (Fe-OM) states that can coat sediment particles, and thus less available. The high affinity of HA for both forms of iron has been reported elsewhere (García-Mina et al., 1995; Tipping et al., 2002; Yan et al., 2013).

Therefore, we attribute the F1 fraction to exchangeable iron, F2 to iron oxo-hydroxides and F3 to the oxidizable pyritic iron and the more reactive forms of organic matter (Nissenbaum and Swaine, 1976; Tessier et al., 1979; Chao, 1984; Åström, 1998; Koretsky et al., 2008; Rodríguez et al., 2009).

In an environment where pyrite is formed at a high rate, pore water (pw) iron concentration tends to be within the micromolar range

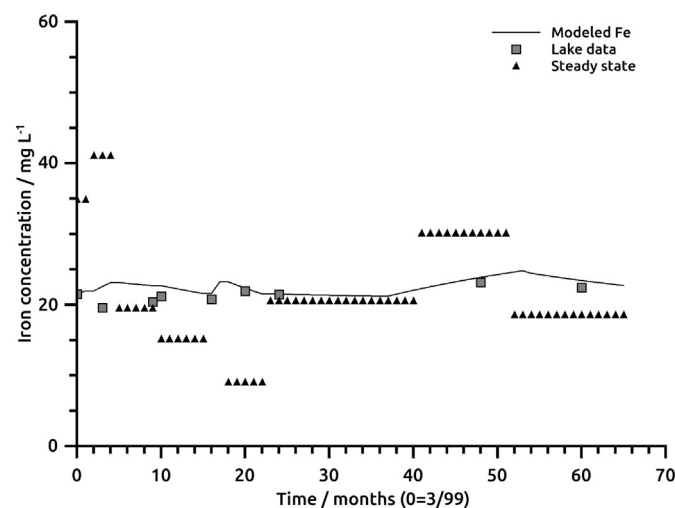


Fig. 4. Observed, expected and steady state iron concentrations of Lake Caviahue (steady state concentration for the eruption period was 73 mg L^{-1}). The time period considered was: month 0 = 03/1999 to month 60 = 03/2004.

Table 5
Saturation indexes for the pre- and post-eruptive periods (years 1999 and 2000).

Pre-eruptive		Post-eruptive	
Mineral	Sat. index	Mineral	Sat. index
Hematite	4.85	Hematite	7.05
Fe(OH) _{2.7} Cl _{0.3}	4.05	Goethite	2.36
Goethite	1.27	K-jarosite	2.32
Lepidocrocite	1.09	Lepidocrocite	2.00
Strengite	0.91	Strengite	2.00
		Ferrihydrite	0.68
		Maghemite	0.36

(Huerta-Diaz and Morse, 1990; Huerta-Diaz and Morse, 1992; Raiswell et al., 1994; Koretsky et al., 2008). In 2010, pw dissolved iron was found to be higher in the sediments at Caviahue. Average Fe²⁺ concentration was 79 ± 26 mg L-pw⁻¹ at NA and 106 ± 53 mg L-pw⁻¹ at SA, while Fe³⁺ concentration was 15 ± 9 mg L-pw⁻¹ and 6 ± 1 mg L-pw⁻¹ for the same sites, respectively. Fe³⁺ accounted for 19% of SA total iron content and 6% of NA (Temporetti, data not published). This high pore-water iron content was also found for Caviahue sediments by Wendt-Potthoff and Koschorreck (2002) and Koschorreck et al. (2008).

High Fe³⁺ content was similarly reported by Krom and Sholkovitz (1978) for anoxic sediments in Loch Duich, a fjord-type estuary in Scotland. Dissolved iron was found to be strongly bonded to low (<1 kD) and high (>1 kD) molecular weight organic matter, such as oxalate, fulvic and humic acids.

In Lake Caviahue, Koschorreck et al. (2008) found high SO₄²⁻ concentration ranging from 384 to 960 mg L-pw⁻¹ and high H₂S concentrations from 0 to 34 mg L-pw⁻¹.

Furthermore, Koschorreck et al. (2008) and Chiacchiarini et al. (2010) found 10⁴ cells mL-pw⁻¹ of iron oxidizers (*Acidithiobacillus ferrooxidans* and *Leptospirillum*-like) and 10⁵ cells mL-pw⁻¹ of sulfur oxidizers (*Acidithiobacillus thiooxidans*) which can explain, along with the low pH values, the high concentrations of Fe and S described above.

Koschorreck et al. (2003) also found that sulfate-reducing conditions predominate over iron-reducing conditions in Lake Caviahue, while for other acidic lakes (where acidity is due to mining and not natural causes) this relationship is reversed (Peine et al., 2000; Blodau and Peiffer, 2003). Koschorreck et al. (2008) observed that a limited reduction rate of 2.3–9.2 nmol h⁻¹ g-dw⁻¹ would occur, and not in all strata, only if free Fe³⁺ was added to the sediments.

Fifty two percent of the total iron content was found to be associated with the residual (F4) fraction and therefore not affected by the oxidation (F3) step. Due to the similarity observed between HA and F4 iron, a Pearson's correlation test was performed with these variables. A strong correlation was found in the arms throughout the vertical profile with coefficients *r* of 0.999 and 0.976 for NA and SA respectively. No correlation (*r* = -0.050) was found for C, even though similar tendencies were observed between the fourth and sixteenth centimeter (Fig. 3).

Luther et al. (1996) predicted the precipitation of HA-Fe complexes when a salt marsh pore water pH dropped below 3.0. Additionally, Young and Harvey (1992) studied seven lakes from south-central Ontario, of which four are acidic and three circumneutral. They found that in the acidic lakes (average pH = 5.31) sedimentary iron was equally distributed among the reducible and OM (alkaline hydrolysis extraction) phases, while in the circumneutral lakes the iron content associated with OM was reduced. Other authors have also searched for correlations between metal and humic substances, although most have studied circumneutral water bodies that are not comparable with Lake Caviahue. Nissenbaum and Swaine (1976) and Reyes-Solís et al. (2009), for example, reported low percentages of total iron associated with organic fraction after alkaline extractions. Devesa-Rey et al. (2010) found a high degree of association between HA and Fe, albeit between HA and the exchangeable (F1) and oxidizable (F3) fractions.

5.2. Water column iron

5.2.1. Iron concentration and partition coefficients

Water column iron concentration in Lake Caviahue has been previously reported to be in the range of 17 to 26 mg L⁻¹ for the lake, and from 23 to 350 mg L⁻¹ for the URA between 1997 and 2006 (Pedrozo et al., 2001; Gammons et al., 2005; Diaz et al., 2007; Pedrozo et al., 2008; Varekamp, 2008 and Varekamp et al., 2009). In the present study, dissolved iron was found to be at the lower limit of these intervals. The data show that differences between the arms and Center are insignificant in comparison to seasonal and inter-annual variations. The concentrations reported for Caviahue are significantly higher than in the circumneutral oligotrophic Andean–Patagonian lakes, which are well below the freshwater world average (Diaz et al., 2007). Iron concentration in Caviahue is also above the guidelines established by Argentine General Environmental Law # 25.675 (0.3 mg L⁻¹ for human and 5 mg L⁻¹ for cattle consumption).

Measurements taken along the transect from the URA discharge point showed that iron concentration decreased by 53% at the coastline and reaches the lake average, a total reduction of 70%, within a distance of 5 m. These data contrast with Varekamp (2008) who in 1997 measured a large plume of poorly mixed water extending into the NA, probably due to significantly higher iron loading at the time.

Partition coefficients were found to be comparable between NA and SA, consistent with total iron content values measured at both sites. Similar values were found for sediments with the same pH values at Lake ML-111, Germany (Friese et al., 1998). The coefficient at the Center of Caviahue was found to be lower than the arms, due perhaps to a variety of factors including the proximity of the site to the URA delta, lower depth and different precipitation and sedimentation rates.

5.2.2. Modeled iron

The observed and predicted iron concentrations for the lake were found to be significantly equal when input loadings were consistently below average. In contrast, no correlation was found for the periods with higher loadings mainly due to the measurements from 03/99 to 06/99. There are two viable scenarios. First, if these two loadings were not constant in time and their impact is minimized, the remainder of the data can be modeled with a 42 months RT (predicted by Varekamp, 2003, 2008) and consistent with a conservative behavior. Second, the high fluxes were constant between the sampling dates, and then it is possible that the real concentration in the lake did not rise due to the precipitation of excess iron at the Agrio River delta. This is consistent with a Fe-buffering system proposed by Ulrich (1981) for water bodies with pH 2–4, without drastically influencing the equilibrium of iron between the dissolved and precipitated phases at the lake basins. Two facts support the proposition. First, the over-saturation indexes for iron minerals for the pre- and post-eruption periods found in the present study as well as in Gammons et al. (2005), should be higher at the URA delta where iron concentration is higher due to the influence of the plume (see Section 4.4.3). Second, sediments at the Center of the lake (Agrio's delta) contained significantly more total iron in the second stratum (see Section 4.3), which may be associated with the high loading values registered before the eruption.

Additionally, schwertmannite formation was observed in the water column in 2008, 2009 (Varekamp, 2015; Agosto and Varekamp, 2016; Rodríguez et al., 2016) and in 2014 and 2015 (Cabrera, data not published). The iron salt was found in filters after passing water from the NA and the SA. The precipitation registered in the years mentioned above also supports the idea of an iron buffer system in the lake.

6. Conclusions

Sedimentary iron is commonly found associated with carbonate precipitates, iron oxides, metal monosulfides or pyrite (depending on the redox state) in circumneutral environments. In the acidic anoxic system

of Lake Caviahue, iron was found to be in strong association with humic acids and pyrite, which can be explained by the pH and Eh conditions of the sediments.

Moreover, total iron content and the partition coefficients indicate that, regardless of how iron is distributed among the chemical phases, deposits at the arms are similar. Different values were found at the center of the lake, which is directly influenced by the URA delta.

Copahue Volcano activity can influence the water body in at least three ways. A pH raise will lead to greater capacity of the sediments to accumulate iron due to the precipitation of iron oxides. A pH decrease will reduce sedimentary iron due to lower pyrite formation rates and a higher solubility of iron. Finally, sediment mixing as a result of seismic activity can lead oxidation and, therefore, iron release from existing pyrite.

Lastly, our results indicate that an iron buffer system exists in the lake; excess iron precipitates when above-average iron inputs are discharged, mostly at the Agrio's delta (over-saturated indexes were found in Section 4.4.3). Consequently, iron concentration in the lake does not follow the model, which predicts higher values when high inputs are registered. The existence of a buffer system is also supported by Varekamp's model (Varekamp, 2003), which accurately predicts iron concentration under conditions of average or below-average loadings, and by the observation of schwertmannite in the water column.

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