



# The volcanic acidification of glacial Lake Caviahue, Province of Neuquen, Argentina

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## ABSTRACT

Lake Caviahue (northern Patagonia, Argentina) is a large glacial lake acidified by volcanic fluids from Copahue volcano. The lake and the feeding rivers were sampled annually from 1997 till early 2006, including the eruptive period of 2000. Lake Caviahue waters evolved over time, with the most concentrated waters in 2000 during the eruptive period, followed by gradual dilution that was interrupted by renewed acidification in 2003–2004. Inversion of the lake water data and application of a dynamic non-steady state model for the lake provides our best quantitative estimates for the variation in element fluxes over the 9-year period. The model flux results agree well with most of the measured fluxes. The Copahue hydrothermal system had gently declining element fluxes between 1997 and mid-1999, although the lake was still becoming more concentrated. About 2–3 months before the 2000 eruption, element fluxes increased strongly, but the hydrothermal fluxes almost shutoff directly after the main eruptive events. The fluxes of several elements recovered post-2001, with an increase in element fluxes in 2003–2004; the lake became more dilute between 2004 and 2006. The intrusion of new magma into the hydrothermal system just prior to the 2000 eruption led to enhanced water rock interaction, with higher concentrations of the rock forming elements in the fluids, and the hot spring flow rate increased as a result of the higher pressure in the reservoir. The fluids became saturated in alunite and jarosite, and they were already saturated with anhydrite. Precipitation of these minerals possibly led to a decreased permeability of the hydrothermal reservoir, leading to the strongly reduced element fluxes just after the eruption. In addition, K, Al and S were retained in the newly precipitated minerals as well, further diminishing their export. The acidification in 2003–2004 may have resulted from a new small intrusion of magma or resulted from seismic activity that created new permeability and fresh rock surfaces for water rock interaction. The volcano is a significant source of toxic trace elements such as F, As, B and Li as well as a nutrient (P) for the local watershed. Monitoring of the hydrothermal fluids in the river that drains Copahue, especially the S/Cl, Mg/Cl and Mg/K values as well as the magnitude of the element fluxes would provide the best information for eruption forecasting for this volcano.

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## 1. Introduction

Volcanic lakes may contain waters with a volcanic component (Delmelle and Bernard, 2000a; Evans et al., 1993; Sriwana et al., 2000; Varekamp et al., 2000) and range from extremely concentrated lakes (crater lakes on active volcanoes, e.g., Christenson, 2000; Delmelle et al., 2000; Rowe et al., 1992a; Pasternack and Varekamp, 1997; Varekamp et al., 2000) to almost pure meteoric water lakes (such as Crater Lake in Oregon, USA, Collier et al., 1990). Occasionally, lakes that are not necessarily volcanic in origin may become contaminated with volcanic effluents, impacting their chemical composition (Delpino et al., 1997). This contamination process commonly also influences the ecosystem of the lake (Pedrozo et al., 2001; Diaz et al., 2007; Beamud et al., 2007), and possibly local drinking-water resources (Delmelle and Bernard, 2000b; Sriwana et al., 1998; Heikens et al., 2005). Temporal compositional variations of such lake waters are a function of fluctuations in the

volcanic input, both in terms of water composition and water fluxes, as well as effects related to the dynamics of the lake system.

The water composition of a large lake with a volcanic input carries a chemical memory of the volcanic influxes of the past, and time series of water composition can provide evidence on the timing and magnitude of changes in the volcanic input. The latter is of interest for volcano monitoring (Giggenbach and Glover, 1975; Martinez et al., 2000; Rowe et al., 1992b; Takano et al., 1994) as well as for predictions on the duration of lake clean-up following a large acid discharge event. Comparison of conservative tracers (e.g., Cl and F if no fluorite saturation occurs) with potentially reactive elements (nutrients like P, redox sensitive elements like Fe and S) may provide insight on element exchange with the lake sediments or biosphere.

The theory for the evolution of lakes towards steady state has been treated in limnology textbooks (e.g., Wetzel, 1983), but was discussed in some detail in relation to lake pollution by Varekamp (1988, 2003). Many volcanic lake studies derive the volcanic input strength of subaqueous inputs from time series of lake water compositions coupled with mass balance or one-dimensional diffusion models for either

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volcanic or non-volcanic inputs (e.g., Rimmer et al., 2005). Well known examples are the studies of Lake Nyos and Monoun (Kling et al., 2005), and Lake Kivu (Schmid et al., 2005) in Africa, which all have subaqueous (“hidden”) volcanic or diagenetic inputs. Many stratified lakes have strong non-volcanic inputs from the sediments (e.g., methane, ammonium) and one-dimensional diffusive models are used with time series of water composition to trace the magnitude of the fluxes and the evolution of the lake water (Rimmer et al., 2005, 2006a,b).

In this study, the water composition of a large lake in Patagonia was analyzed over a ~9-year period, the volcanic input fluxes into that lake were determined once or twice each year, and a dynamic model was developed for the lake. Inversion of the compositional data of the lake waters was used to create best estimates for the mean volcanic element flux variations over time, and the calculated mean fluxes were compared with the annually observed element fluxes. The volcanic element flux variations are subsequently interpreted in terms of volcanic source flux variations, water rock interaction processes, and “best choice” parameters for eruption forecasting. The lake modeling also provides insights into the time frame of lake water contamination and clean-up.

## 2. Regional setting

Copahue volcano (38 S, 71 W) is an active volcano on the border of Argentina and Chile (Bermudez and Delpino, 1995; Delpino and Bermudez, 1993, 1995, 2002) with an extensive volcano–hydrothermal system and associated geothermal system (Casertano, 1964; Fehn et al., 2002; Gammons et al., 2005; Martini et al., 1997; Pesce, 1989; Varekamp et al., 2001, 2004). The most recent magmatic eruption started in July 2000 and continued intermittently till early 2001 (Naranjo and Polanco, 2004; GVN 2000a,b). Abundant fine-grained ash was distributed throughout the region, some of it with clumps of solidified native sulfur (Gomez et al., 2002). Ash beds on the slopes of Copahue still showed yellow sulfur coatings in 2003 and 2004, evidence for adsorbed sulfur of hydrothermal origin (Delpino and Bermudez, 2002).

Copahue volcano had an active crater lake (sample code CPL) between 1997 and 2000 (~200 m in diameter, maximum 35 m deep, Ouimette, 2000; Varekamp et al., 2001, 2004), which was ejected and evaporated during the 2000 eruptions, but re-established itself soon after. The crater lake is sometimes in convective state with suspended sediment, other times quiet with a deep green colour and floating yellow sulfur. On the east flank of the mountain just below the lake (Fig. 1) an acid hot spring (local name: *el Vertedero*, sample code CP) emerges that feeds a river system, the Rio Agrio. The headwaters of the Upper Rio Agrio (river section on the mountain, URA) are *el Vertedero*

as well as several smaller hot spring fields, some emerging from below the local summit glacier. Some crater lake seepage and spillage may possibly also contribute to some of these subglacial springs. The hydrothermal fluid output of the volcano consists of the outflows of the various hot springs, of which *el Vertedero* is the largest and possibly minor crater lake seepages. Details of the chemical composition of these hot springs and lake waters is given in Pedrozo et al. (2001), Gammons et al. (2005) and Varekamp et al. (2001, 2004). Over a trajectory of about 14 km the river descends from the volcano into the foothills and then enters the large plain of the Agrio caldera (Melnick et al., 2006), also known as the Caviahue caldera (Varekamp et al., 2006), and discharges through a floodplain with a small delta into Lake Caviahue (sample code CVL).

Lake Caviahue consists of two drowned river arms, glacial canyons or faultbounded troughs (Melnick et al., 2006). The URA and Agua Dulce, a glacial meltwater river, are the main water inputs for the lake. The peninsula in between the two lake arms is covered by lava flows that tilt up towards the two lake arms (Varekamp et al., 2006), suggesting that there were once topographically high areas where the lakes exist now (possibly ice?). There is no connection between the southern lake arm and the southern caldera outlet, and the exact origin of the steep valleys that form the lake basin is unclear. The lake drains through the Lower Rio Agrio (LRA) on the eastern side of the north arm through a narrow opening. This river leaves the caldera further to the North, where it joins with the Rio Trollope and then after exiting the caldera forms a large cascade (La Salta). In this area, a thick floc of Fe-oxides with organic matter covers the riverbanks and forms ‘bubbling floats’ on the water. The yellow mineral is most likely Schwertmannite, a ferric sulfate hydrate stable at pH values of about 3–3.5. The river flows down the gentle slope of the Caviahue volcanic complex to join the Norquin river (south of El Huecu) and then, as a much more dilute stream, flows south towards the town of Loncopue (Fig. 1, for locations see map in Gammons et al., 2005). From there, the river flows along Las Lajas ultimately to Neuquen, the provincial capital, and then flows further to the Atlantic Ocean as the Rio Neuquen. Volcanic influences (red precipitates on boulders) are still present near Loncopue, which is about 30 miles in a straight line away from the lake.

The climate around Caviahue is harsh with fierce winds and up to 4 m of snowfall during the winter. Almost every day during the afternoon a strong wind stirs the upper part of both lake arms. There is no record that the lake froze over during the winter months. Some Agua Dulce waters drift along the Caviahue beach to the south and then mix with the URA plume. The nutrient balance of the lake, including contributions from a small sewage treatment plant near the Agua Dulce, was discussed by Pedrozo et al. (2001, 2008-this issue);

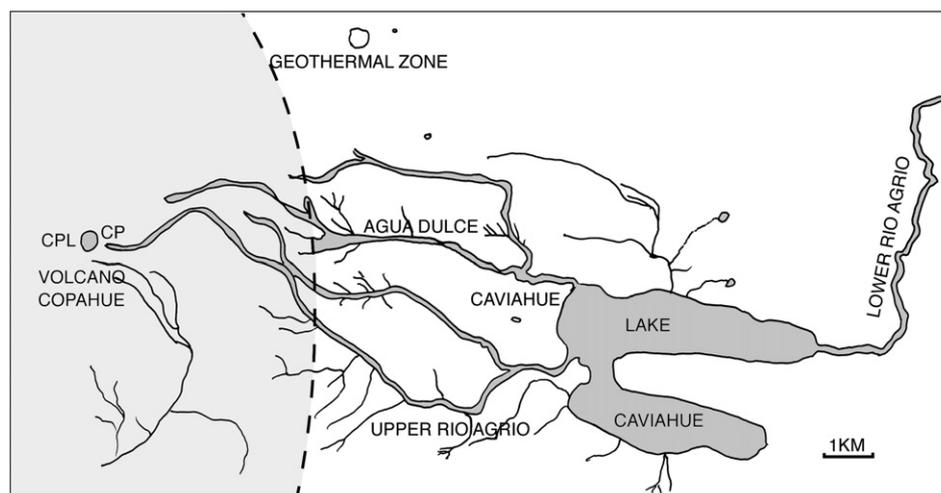


Fig. 1. Geography of the area around Lake Caviahue, with Volcan Copahue, the URA, Lake Caviahue with its two E–W arms, and the LRA.

(Diaz et al., 2007; Beamud et al., 2007). Birds land upon the water but rarely (pH has varied from 2.1 to 2.7 over the last decade) and near the inflows of glacial streams dead fish are common, which probably died the moment they entered the acid waters. A variety of life forms occur in these acid waters (Wendt-Potthoff and Koschorreck, 2002). Sediment grab samples had a profound H<sub>2</sub>S smell, indicating that diagenetic sulfate reduction in the sediment column is a common process (Koschorreck et al., 2008–this issue).

The main vegetation around the lake consists of *Auracaria Auracana* trees (Monkey puzzle trees, Bekessy et al., 2002); their debris and leaves constitute a significant flux of terrestrial organic matter into the lake. The rivers carry volcanic sediment into the lake (glacial debris, hydrothermally altered clays). During and after the 2000 eruptions of Copahue volcano, the lake waters were charged with fine-grained ash from direct fall-out and from river import. Data and models of Lake Caviahue were presented before by Pedrozo et al. (2001), Wendt-Potthoff and Koschorreck (2002), Varekamp et al. (2001) and Varekamp (2003), and the rare earth element geochemistry of the Caviahue watershed was treated in detail by Gammons et al. (2005).

### 3. Sampling and analytical methods

Waters from Lake Caviahue, the URA and LRA as well as a variety of streams and ponds were sampled between 1997 and March 2006 on an annual or bi-annual basis (January, March or November). Data from other studies for this period were compiled as well (Parker et al., 2008–this issue; Pedrozo et al., 2008–this issue; Gammons et al., 2005). Water samples were filtered (0.20 μm) and pH and temperature were measured in the field with a digital meter. Concentrated URA waters were diluted in the field by adding 1 ml or 2 ml to a pre-measured amount of 50 ml distilled water (dilution 26 and 51 times).

Water samples in Lake Caviahue were collected from a raft with a plastic VanDorne sampler with a stainless steel messenger. Water samples were collected at 10 m intervals from surface to bottom using a simple mechanical winch. The water temperature and pH were measured (calibrated at pH 4 and 7) after the water sample was retrieved at the surface. The samples were stored in new HDPE 250 ml bottles and labeled with date, lake arm and water depth.

The URA and LRA water fluxes were measured between 1997 and 2004 with an “Oceanic” brand flow meter, a mechanical device with a small impeller. The 2006 measurements were done with a flow meter with a magnetic sensor on an impeller and digital read-out. The flow rate was measured in river cross sections about 10 cm above the river bottom. The depth of the sites of measurements in each cross section was recorded and from water flow and cross sectional area the water flux was determined. Repeat measurements indicate variations up to 15% depending on riverbed morphology. Cross calibration with another flow meter suggested that at low water flow our early meter may have given about 10% low readings, but at higher flow rates the measured values were very close (within a few %). The LRA water flux measurements are less precise than those from the URA because the LRA is very shallow, with many large emerged boulders, and it has very high water flow velocities. Water samples were collected at the sites of the flux measurements at the same time in order to determine the element fluxes. Water samples were stored at Wesleyan University prior to analyses, and showed no evidence for algal growth or precipitates. Some 2003 samples from the URA precipitated a red–yellow flocculate upon dilution, presumably Schwertmannite. These samples were diluted with HCl prior to analyses to prevent the flocculation.

Waters were analyzed for F, Cl and SO<sub>4</sub> by Ion Chromatography (Dionex system 600) using both electrolytic and acid conductivity suppression. Standards for instrument calibration were Dionex commercial standards as well as homemade F–Cl–SO<sub>4</sub> standards prepared from salts (NaCl, NaF, CaSO<sub>4</sub>). In addition, a validation standard of 1992 Maly Semiachik crater lake water was used, which has been analyzed by many laboratories (Takano et al., 2000). Some Cl analyses were cross checked

with Cl specific electrode measurements, which showed very good agreement (Ouimette, 2000). A subset of samples was analyzed by ICP-AES for bulk S as well as by barite precipitation and gravimetry. Subsequently, the majority of samples was re-analyzed by ICP-AES for bulk sulfur and these data are used here. Cations were analyzed by ICP-AES at Wesleyan University and by ICP-AES and ICP-MS at SGS commercial laboratories (formerly XRAL laboratories, Toronto, Canada). The runs at Wesleyan University had standards that were matrix-matched with H<sub>2</sub>SO<sub>4</sub> and HCl solutions, and calibration standards were diluted commercial standards in the matrix solution. Cross references of samples analyzed by both laboratories gave generally satisfactory results. The analyses of Na were in some series significantly different between ICP-AES and ICP-MS analyses and we used mainly the ICP-AES results. The waters were also analyzed for a set of trace elements at SGS by ICP-AES and ICP-MS. The two instrumental techniques again gave significant differences for several elements, and in general we used the ICP-MS data for most trace metals, whereas Rb, Sr, and Mn showed satisfactory agreement between ICP-AES and ICP-MS. Rare earth elements were determined by ICP-MS and agree well with the data of Gammons et al. (2005). The 1997–2000 samples have been re-analyzed for most elements in runs with the 2000–2006 samples to provide internal consistency. The final results differ in some instances slightly from earlier presented data (Varekamp et al., 2001, 2004; Varekamp, 2003) because of these re-analyses. Comparison with analytical data from other studies on samples taken from the same locations indicates a good agreement for the major elements (Parker et al., 2008–this issue; Gammons et al., 2005).

### 4. Lake Caviahue

Lake Caviahue has two east–west arms, each with a maximum depth of about 90 m, and the lake has a surface area of 9.22 km<sup>2</sup> and a volume of 0.474 km<sup>3</sup> (Rapacioli, 1985). The lake is stratified during the austral summer, with temperatures reaching up to 18 °C in the surface waters, a thermocline around 35 m depth and bottom waters with a temperature range of 5–9 °C (Fig. 2). During the austral winter, the lake is fully mixed, a situation that may persist from April till November. The URA inflow forms a large plume of glacial meltwater with a dissolved volcanic component, and the mixing behavior of the plume and the lake waters varies strongly with the season. Most of the time the water seems to travel largely along the northern arm and then out through the LRA. The waters from the Agua Dulce enter at the northwest end of the northern lake arm and drift both south and east into the lake. As a result, the waters along the beach in Caviahue village tend to be slightly more dilute as a result of the local mixing with the Agua Dulce glacial melt water.

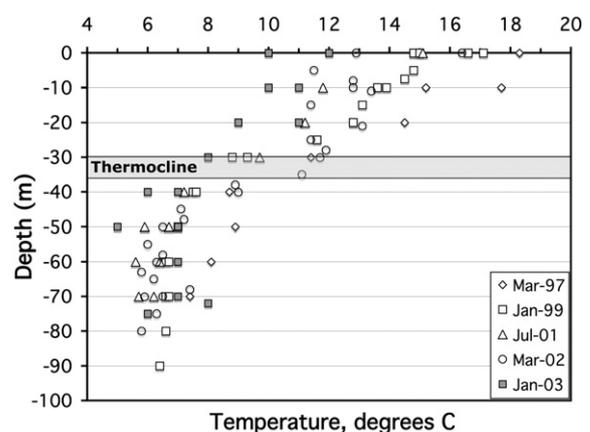


Fig. 2. Depth–temperature profiles for Lake Caviahue between 1997 and 2004. The thermocline occurs around 35 m depth in the Austral summer season.

Mean river water fluxes were estimated by Rapacioli (1985) and Pedrozo et al. (2008-this issue), and flow data were obtained for this study. The flow measurements were done largely in January and March, with a few datapoints in July, so the full spectrum of flow values has not been sampled. The lake level varies by several m with the seasons, which influences the LRA discharge rate. The available time series of URA fluxes shows an oscillating discharge pattern (Fig. 3), with high flow rates in the austral late winter/early spring, and lower rates in the summer; the high flow rates in the austral winter are strongly under represented in the data series. I fitted two oscillating curves through the data that approximately match the data: one that peaks at  $2.9 \text{ m}^3/\text{s}$  and one that peaks at  $3.9 \text{ m}^3/\text{s}$ , both with low values of  $0.4 \text{ m}^3/\text{s}$ . From the areas under the oscillating curves I calculated the mean annual URA water flow at  $\sim 66\text{--}83 \text{ 10}^6 \text{ m}^3/\text{year}$ . The main fresh water inlet to the lake (Agua Dulce) carries  $\sim 38 \text{ 10}^6 \text{ m}^3/\text{year}$ , for a total river input into Lake Caviahué of  $103\text{--}120 \text{ 10}^6 \text{ m}^3/\text{year}$ . Small glacial meltwater streams feed the lake on the south side and spring-fed pools and small rivers feed the lake on the north side in the plains of the Caviahué caldera. Local lore suggests that very minor subaqueous hot springs may exist in the lake. Melting of the winter snowpack (up to several m thick) creates direct discharge from the land to the lake. Direct precipitation on the lake is  $\sim 16 \text{ 10}^6 \text{ m}^3/\text{year}$  (assuming  $\sim 1.8 \text{ m}/\text{year}$  precipitation; Rapacioli, 1985) and evaporation in the dry and windy climate of the Patagonian desert is estimated at  $\sim 11 \text{ 10}^6 \text{ m}^3/\text{year}$  (evaporation rate of  $1.2 \text{ m}/\text{year}$ ; Rapacioli, 1985).

The water residence time of the lake was estimated by Rapacioli (1985) at 2.6 years, which implies a total annual water influx of  $\sim 180 \text{ 10}^6 \text{ m}^3/\text{year}$ . The riverine water influx would be  $164 \text{ 10}^6 \text{ m}^3/\text{year}$ , with an evaporation over river input value ( $E/I$ ) of about 6%. A study of Patagonian lakes further south (Mayr et al., 2007) indicated a local  $E/I$  of  $\sim 60\%$ , but rainfall is much lower in that southern region. The melting ice cap of Copahué also provides an enhanced river water flux for Lake Caviahué compared to these southern Patagonian lakes. Stable isotope data from Lake Caviahué, the URA and local meteoric waters (Varekamp et al., 2004) suggest an  $E/I$  value of  $\sim 5\text{--}10\%$  for Lake Caviahué (Varekamp, in preparation). The mean river water flux calculated from our measurements and curve fits ( $103$  to  $120 \text{ 10}^6 \text{ m}^3/\text{year}$ ) accounts for  $\sim 62\text{--}74\%$  of the estimate by Rapacioli (1985). The LRA discharges about  $86\text{--}111 \text{ 10}^6 \text{ m}^3/\text{year}$  (mean of total available data, Fig. 3), and the peaks in LRA discharge rate are larger than and lag the peaks in the URA inflow rate. The LRA discharge rate is determined by the lake level, which gradually builds up over the period of high river input rates and precipitation. The sum of the mean LRA flow rates and the evaporative water loss ( $97\text{--}122 \text{ 10}^6 \text{ m}^3/\text{year}$ ) is very close to

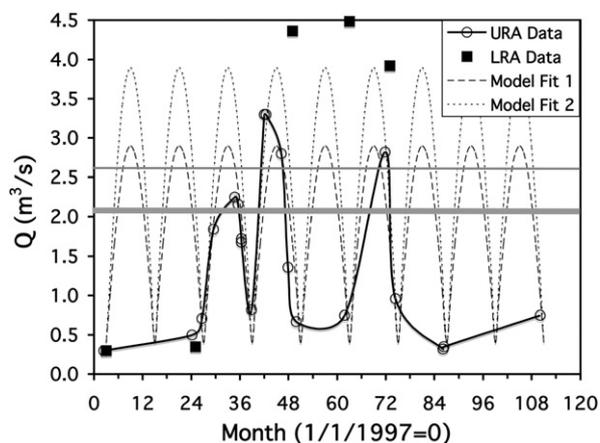


Fig. 3. River flow data for the URA near the bridge in Caviahué and LRA at the northeastern lake exit. The dashed oscillating curves are model fits that simulate the seasonal variation in river discharge and broadly fit the available data. The mean water flux for the low estimate (model 1 peaks at  $2.9 \text{ m}^3/\text{s}$ ) is  $2.1 \text{ m}^3/\text{s}$ , whereas model fit 2 uses a peak value of  $3.9 \text{ m}^3/\text{s}$  and has a mean of  $2.6 \text{ m}^3/\text{s}$ . Both models have low values of  $0.4 \text{ m}^3/\text{s}$ , in agreement with the data.

the range of input values, suggesting that on a mean annual basis the lake is close to steady state for water. The total mean water input and output estimates lead to a mean water residence time of 3.5–4.0 year, with variation through the seasons. In conclusion, the data from all available studies suggest that the water residence time of Lake Caviahué ranges from 2.6 to 4.0 years, depending on seasonal lake level and river water fluxes. The evaporative flux is probably not much more than 5–10% of the river water flux, indicating that the residence times of conservative elements are similar to the water residence time. Varekamp (2003) suggested a residence time for Mg of  $\sim 4$  years, based on measured Mg influxes and variations in Mg concentration in the lake waters between 1997 and 2000, in close agreement with the water residence time given above. The residence time estimates derived from element fluxes and lake water concentrations are not influenced by seasonal variations in precipitation and river water discharges: if the URA water flux increases, the element concentrations drop as a result of dilution. Short term variations in the element fluxes from the volcano through the hot springs are the main source of uncertainty in that approach.

## 5. Chemical results

Results of lake water analyses (142 samples, representative data in Tables 1a, 1b) for the major rock forming elements (RFE) and volcanogenic elements (VE) show that Lake Caviahué has the highest RFE concentrations for Al (20–36 ppm), followed by Fe (17–35 ppm), Ca (18–28 ppm), Mg (13–24 ppm), Na (10–28 ppm), Si (11–17 ppm) and K (6–8 ppm). The pH values of the lake waters have varied from 2.1 to 2.7 (Table 1a). The Cl concentrations ranged from 63 to 118 ppm and sulfate concentrations were between 253 and 730 ppm. The F concentrations were 6–11 ppm, well above the WHO drinking-water standard (WHO, 1996) of 1.5 ppm. Trace element concentrations are 150–600 ppb P, 700–1000 ppb Mn, 10–50 ppb Ni, 10–100 ppb Cu, 150–275 ppb Sr, 70–110 ppb Ti, 30–85 ppb V, 50–250 ppb Zn, 30–40 ppb As and 40–50 ppb B. The Ba concentrations vary from 10–80 ppb, with no simple relationship with sulfate concentrations (Table 1b).

The field data show that the lake was thermally stratified during most of our sampling trips (Fig. 2), except during November 1999, when the lake was close to vertically homogeneous in temperature. Despite the thermal stratification, the lake was chemically close to homogeneous in most sampling periods for most elements, although in some years the very bottom layer was slightly more concentrated than the surface waters. The pH values decreased with depth, to reverse again in the lower 20 m, and also showed small but significant differences between the Northern and Southern lake arms (Fig. 4). Time and depth trends for Al show small increases in Al concentration with depth and a secular trend with increasing Al from 1997 to 2001, followed by a decrease (Fig. 5). Water samples taken from the lake surface near the beach in Caviahué are more dilute than samples from the more central part of the lake as a result of the nearby glacial melt water input from the Agua Dulce. Similarly, the URA river water plume is initially poorly mixed inside the lake in the inflow zone, and a suite of such more concentrated ‘river plume’ samples was collected in 1997.

The total dissolved solids (TDS) of Lake Caviahué waters varied over the course of the 9-year study period in response to the changes in hydrothermal output of Copahué volcano (Fig. 6). We distinguish the pre-eruptive period (1997–December 1999), the eruptive period of mid-2000 to early 2001, and the post-eruptive period from 2001–2006. During the eruptive period, the input of RFE as well as VE increased (Varekamp et al., 2001), leading to the highest element concentrations of the lake waters in mid-2000 (Fig. 6). After the main phase of the 2000 eruption, the hydrothermal system diminished its output through the acid hot springs greatly, and the springs became more dilute as well. The lake showed significant increases in concentration again in 2003–2004, possibly in response to magmatic or seismic activity inside the mountain, but then became more dilute again towards 2006. Some RFE concentrations slowly increased after the 2000 eruptions (Fe, Mg,

**Table 1a**

Major element composition of Lake Caviahue waters between 1997 and 2006. All element data in ppm, except pH. Blank spaces: not determined

Sample	Date	pH	F	Cl	SO <sub>4</sub>	Al	Fe	Mg	Ca	Na	K	Si	S/Cl
CVLN-10	3/14/97	2.5	10.3	88	335	28.6	18.7	13.9	19.5	13.1	5.9	17.4	1.27
CVLN-50	3/14/97	2.5	10.0	81	345	27.8	18.3	13.7	19.3	13.2	5.9	17.4	1.42
CVLS-30	3/18/97	2.5	10.9	80	327	26.4	17.3	13.3	18.6	10.7	5.6	17.0	1.36
CVLS-40	3/18/97	2.6	10.6	81	317	24.9	16.7	13.0	18.1	9.9	5.3	17.3	1.30
CVLS-30	01/8/99	2.5	10.8	91	474	30.4	19.9	14.2	19.9	13.1	7.1	13.8	1.74
CVLS-60	01/8/99	2.4	10.1	92	441	30.4	19.6	13.9	20.1	13.2	6.6	14.0	1.59
CVLS-70	01/8/99	2.4	10.3	90	437	30.3	19.4	13.9	20.3	13.0	6.8	13.9	1.62
CVLS-0	11/99	2.5	9.1	91	450	30.6	20.4	14.2	21.5	12.3	7.7	14.2	1.65
CVLS-70	11/99	2.4	10.4	99	476	33.5	22.1	15.1	23.1	13.2	8.3	14.6	1.60
CVLS-0	07/06/00	2.2	8.7	104	476	26.1	18.7	13.7	22.0	12.2	8.2		1.52
CVLN-0	07/06/00	2.3	9.5	94	554	29.0	22.5	16.8	23.7	13.3	7.0		1.97
CVLN-0	07/06/00	2.2	10.4	107	578	32.8	23.3	16.1	23.1	14.5	7.6		1.80
CVLN-70	07/06/00	2.1	12.4	117	713	35.8	34.7	24.2	28.3	15.5	8.3		2.02
CVLN-82	07/06/00	2.2	12.4	118	730	35.6	33.7	23.8	26.6	16.2	8.9		2.06
CVLS-10	01/15/01	2.3	9.0	91	478	30.2	21.2	18.0	22.8	13.2	6.8	12.4	1.76
CVLN-30	01/16/01	2.4	8.9	90	482	30.0	21.3	17.3	23.7	13.2	6.4	12.8	1.79
CVLN-40	01/16/01	2.4	8.2	84	450	30.5	22.0	18.0	23.8	13.3	6.8	12.5	1.79
CVLN-50	01/16/01	2.4	9.1	92	502	30.1	21.7	18.4	24.1	13.4	6.9	12.4	1.82
CVLN-10	03/20/02	2.6	8.0	79	437	26.1	22.7	20.8	23.0	13.0	5.8	12.4	1.85
CVLN-40	03/20/02	2.5	8.1	79	426	26.9	22.6	20.2	22.6	12.6	5.8	12.2	1.80
CVLN-75	03/20/02	2.5	8.3	82	449	27.4	23.2	19.5	23.0	12.9	6.0	12.5	1.83
CVLS-38	03/20/02	2.4	7.8	77	452	25.8	22.3	17.9	22.2	12.4	5.9	13.5	1.94
CVLS-48	03/20/02	2.4	7.7	78	432	26.5	21.3	17.1	22.1	12.3	5.9	13.3	1.85
CVLN-50	01/22/03	2.4	7.2	74	371	22.5	20.7	18.9	18.7	13.0	5.3		1.67
CVLN-70	01/22/03	2.5	7.4	72	368	24.0	22.0	19.8	19.7	13.2	5.7		1.70
CVLS-60	01/23/03	2.7	7.2	72	405	23.0	20.3	18.1	20.3	13.3	5.3		1.88
CVLS-72	01/23/03	2.6	7.2	72	393	24.1	21.1	18.7	19.7	13.5	5.6		1.81
CVLN-20	03/12/04	2.3	8.5	86	350	23.2	22.7	24.3	19.8	14.1	4.9		1.35
CVLN-40	03/12/04	2.4	8.2	76	334	21.1	22.3	21.7	21.8	14.6	4.6		1.46
CVLN-50	03/12/04	2.4	7.8	75	329	20.5	21.8	21.0	19.2	13.2	4.6		1.47
CVLN-0	11/21/04	2.6	7.5	80	329	21.8	22.4	22.2	20.0	14.7	4.6		1.37
CVLN-0	03/16/06	2.5	7	7	300	21.5	19.3	22.6	21.4	13.5	4.7		1.11
CVLN-50	03/16/06	2.6	6	64	272	19.9	18.5	21.0	19.7	12.5	4.0		1.04
CVLS-0	03/16/06	2.7	6	63	253	19.4	18.3	20.8	19.4	12.3	4.1		1.02

**Table 1b**

Trace element data for Lake Caviahue between 1997 and 2004. Mn analyses are in ppm; all others are in ppb. Blank spaces: below detection

Sample	Date	Mn	Sr	Sc	Ti	V	Ni	Cu	Zn	Cr	Co	As	Y	Ba	B
CVL-0	3/1/97	0.8	202	5	101	58	10	13	5.6	10	10		12	15	130
CVLS 60	1/12/99	0.8	194	5	118	54	13	17	54	16			10	13	36
CVLN 80	1/12/99	0.8	207	5	132	60	13	13	54	16		35	10	13	42
CVLN 80	11/1/99	0.8	207	5	145	60	20	24	147	16		33	10	50	54
CVLN 80	7/1/00	1.1	276	7	199	85	37	63	99	27	18	39	14	20	39
CVLS-0	7/6/00	0.7	210	5	140	50	13	13	39	10			7	10	0
CVLN 75	1/1/01	0.9	219	5	146	63	23	13	49	18	12	40	11	16	30
CVLS 60	1/1/01	0.9	226	5	152	62	19	23	49	17	10	36	11	15	28
CVLN 60	3/2/02	1.0	199	4	116	54	24	20	129	15	12		11	52	57
CVLS 60	3/2/02	0.9	194	4	124	56	23	21	126	15	11		11	56	56
CVLN 75	1/1/03	1.0	170	4	101	46	47	19	135	13	11		10	78	55
CVLS 60	1/1/03	0.9	166	3	90	46	23	19	113	12	11		10	76	48
CVLS-0	3/13/04	1.0	160	3	70	40	20	11	58		10		9	10	
CVLN-0	11/21/04	1.0	155	4	60	40	20	9	57				9		

Na, Ca), whereas Cl, F and SO<sub>4</sub> decreased over the last few years together with the K and Al concentrations. The groups of data of the pre-, syn- and post-eruptive lake waters show these compositional trends quite clearly (Fig. 7a and b). In the early post-eruptive period, the cation ratios changed strongly, but in 2006 a simple dilution trend with approximately constant Fe/Al values emerged (Fig. 7b).

Secular trends for the individual cations and anions show an increase in most elements over the period 1997 to 1999, with more diverse trends between 2000 and 2006. The pH of the lake remained broadly constant between 1997 and late 1999, to fall steeply during 2000 and then the lake became less acidic, a trend that reversed again in 2004 (Fig. 8) and then became more dilute again towards 2006.

The analytical data of the URA and LRA (Tables 2a, 2b), Agua Dulce and various other ponds and rivers (Ouimette, 2000; Gammons et al.,

2005) show widely varying concentrations for major elements, related both to fluctuations in the composition of the feeding springs at the volcano summit as well as degree of dilution with the season. Much of the variation in the URA water composition is the result of dilution, but the various springs and tributaries to the river supply waters with different element ratios, creating a complex mixture that varies in composition with time. Water flux measurements and chemical analyses from samples taken at the bridge in Caviahue and from the LRA near the northern lake exit provided the element flux data (Table 3).

The compositional variation in Lake Caviahue is thus related to changes in the quantity and composition of the input fluids from Copahue volcano. In addition, as a result of the large mass of the lake, the compositional variation of lake waters is also related to non-steady state effects and the lake water composition carries a memory

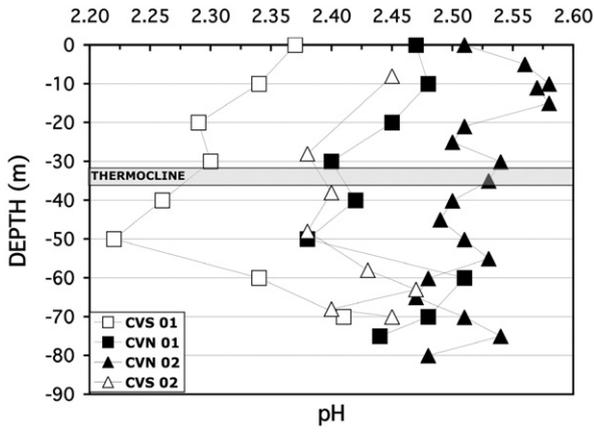


Fig. 4. Depth–pH data for Lake Caviahue showing pH variations with depth, differences between the N and the S arms of the lake, and the increase in pH in 2001–2002 and in 2005–2006. CVS: Lake Caviahue southern arm, CVN: Lake Caviahue northern arm.

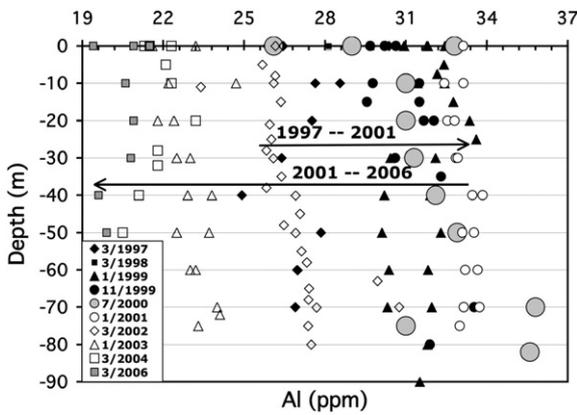


Fig. 5. Depth–Al data for Lake Caviahue, showing minor trends with depth and an increase from 1997 to 2001 followed by a rapid decrease, culminating in the relatively dilute state of 2006.

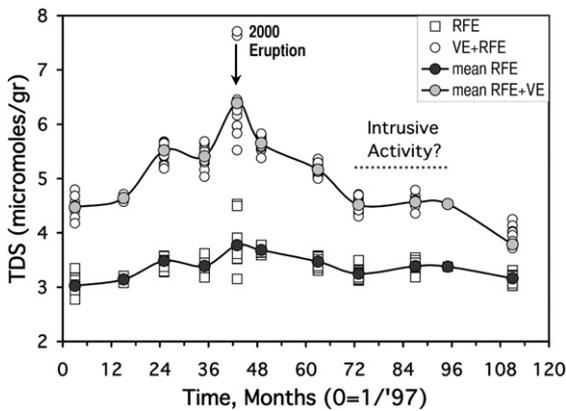


Fig. 6. Time trends in total dissolved solids derived from rock dissolution (RFE) and volcanogenic elements (VE), showing a peak in TDS around the eruption of 2000, followed by a general decline with a modest second peak in 2003–2004.

of past element input fluxes and their variations. I present here a quantitative approach to model the secular variation of the composition of Lake Caviahue waters and the reconstructed variations in element input fluxes. The calculated mean element fluxes are

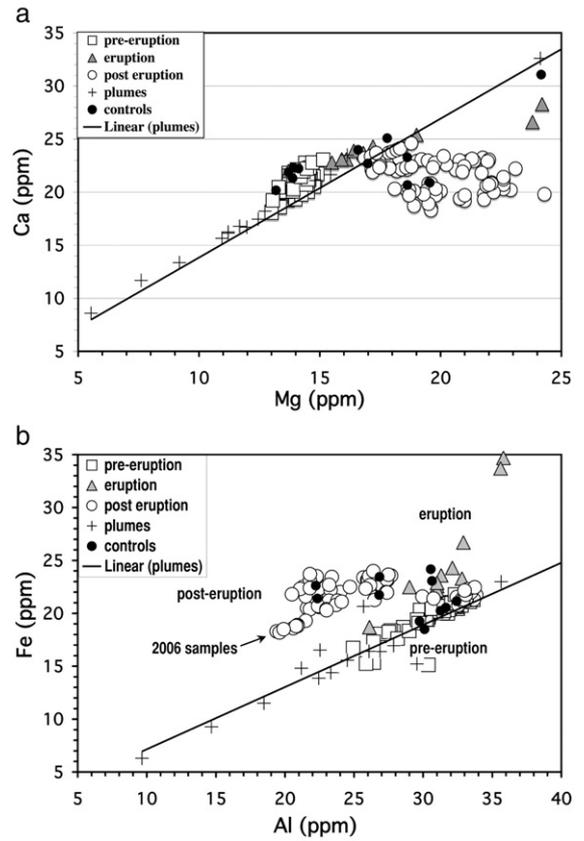


Fig. 7. Compositional trends in the lake before, during and after the 2000 eruption. The “plume” samples refer to the poorly mixed URA and Agua Dulce plumes in the lake in 1997. a. The Ca and Mg concentrations both increased during the eruption, whereas after the eruption the Ca concentrations remained roughly constant, while Mg increased over time. b. The Al and Fe concentrations both increased during the eruption, while after the eruption the Al concentrations fell rapidly, whereas the Fe concentrations remained roughly constant or increased slightly. The 2006 data show the general dilution of the lake while the Fe/Al values remain constant.

then compared with the instantaneous measured fluxes from the river flow data.

### 6. Model of the compositional trends in Lake Caviahue

The compositional trends in Lake Caviahue over time are the result of two main processes: evolution towards steady state of the lake

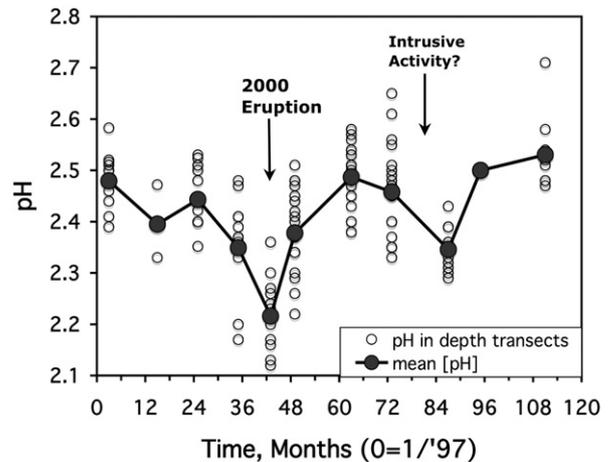


Fig. 8. Time–pH trend for Lake Caviahue with more acid conditions during the 2000 eruption, the subsequent increase in pH, and a decrease in 2004, followed by further dilution in 2006 (the mean [pH] values are averages of the H<sup>+</sup> concentrations, not the mean of the pH values).

**Table 2a**

Major element composition (ppm) of the URA and LRA. Blank spaces: not determined. pH values of URA samples are all <2

Date	F	Cl	SO <sub>4</sub>	Na	Mg	Al	K	Ca	Fe	Si	S/Cl
<b>URA</b>											
3/16/97	198	1656	7736	184	162	618	128	236	350	48	0.10
1/7/99	46	950	4744	102	98	281	65	171	173	36	0.10
1/12/99		1034	5148	95	105	295	64	173	181		0.14
11/25/99	15	178	1059	24	25	55	14	49	31	15	1.03
7/6/00	13	129	1223	33	133	76	7	88	125		0.35
1/13/01	13	163	907	27	58	45	9	72	34	23	0.25
3/1/02	36	280	1167	26	71	44	5	45	53	19	0.38
1/21/03	17	165	460	30	62	27	6	44	23	20	0.27
3/12/04	129	1360	3044	234	362	301	24	189	333		0.20
3/14/06	49	591	1544	92	118	169	22	123	105		0.10
<b>LRA</b>											
1/99		98	532	13	15	33	7	22	21	13	0.13
8/00		93	436	11	14	31	7	22	20	14	0.15
1/01		83	523	13	16	26	7	21	23	12	0.15
3/02		73	450	10	17	24	6	17	23	12	0.19
1/03		67	405	9	16	20	4	15	20	12	0.23

**Table 2b**

Trace element data of the URA (Mn in ppm, rest in ppb). Blank spaces: below detection

Date	Mn	Sr	Sc	Ti	V	Ni	Cu	Zn	Cr	Co	As	Y	B
1/1/99	6.0	1830	60	1550	583	120	49	313	170	54	456	89	375
11/1/99	1.8	412	11	268	107	29	14	163	29	14	90	21	97
7/1/00	3.9	615	22	577	219	163	127	232	81	92	88	42	100
1/1/01	3.3	357	8	58	67	85	108	123	23	55		30	87
3/4/02	3.3	338	7	52	77	45	30	262	11	32	52	32	91
1/3/03	3.0	267	5			27	11	130		19		20	55
3/11/04	12.2	1200	65	170	600	80	32	845	100	50	640	90	
11/22/04	2.1	258	8	40	70	20	9	91	20		70	16	

reservoir and variations in the element input fluxes. The first one can be understood by considering a clean lake that at some time starts to become contaminated by a new input. Over time the concentration of the contaminant will increase until the amount of contaminant that reaches the lake with the input equals the outflux of that particular element in the lake outflow (several residence times needed to reach a condition close to an approximate steady state). The evolution towards steady state is also a function of the mixing behavior of the lake waters. Equations for the evolution towards steady state in stratified lakes were developed by Varekamp (2003), with a more general derivation for a fully mixed lake in Varekamp (1988), which

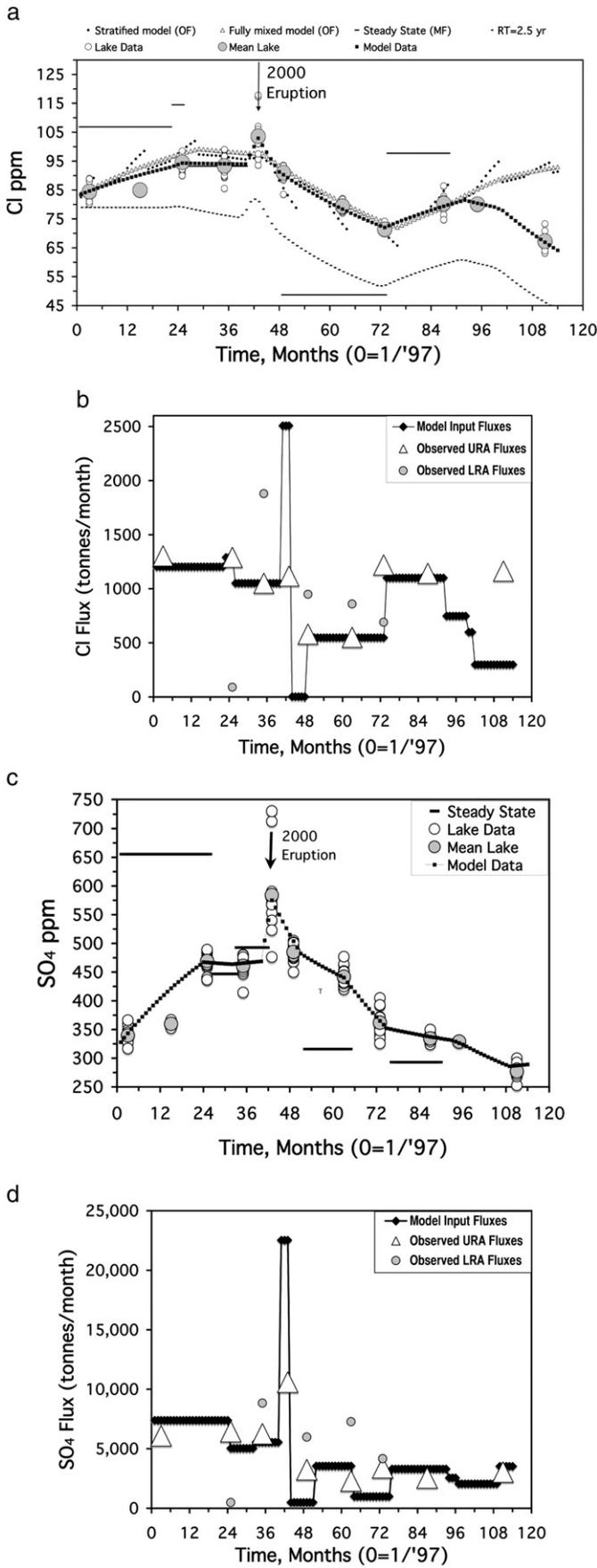
**Table 3**

Upper Rio Agrio and Lower Rio Agrio water (*Q*) and element fluxes as measured at the bridge in Cavihue and at the northeastern lake outlet (date: month/day/year; units: t/m = tonnes/month). Blank spaces: measured concentrations below detection (Mn) or not determined (F)

	<i>Q</i> (m <sup>3</sup> /s)	F (t/m)	Cl (t/m)	SO <sub>4</sub> (t/m)	Na (t/m)	Mg (t/m)	Al (t/m)	K (t/m)	Ca (t/m)	Fe (t/m)	Si (t/m)	Mn (t/m)
<b>URA</b>												
3/16/97	0.3	156	1306	6099	145	128	487	101	186	276	38	7
1/14/99	0.5	58	1292	6442	128	132	375	84	224	230	45	8
11/25/99	2.3	89	1053	6262	142	148	323	84	290	185	87	
7/6/00	3.3	113	1119	10,604	289	1150	659	63	765	1085		35
1/12/01	1.4	45	583	3242	97	206	160	32	257	122	82	
3/10/02	0.8	71	552	2300	51	140	86	10	89	105	64	
1/15/03	2.8	124	1221	3404	222	461	196	45	323	172	151	
3/12/04	0.3	108	1144	2560	197	304	253	20	159	280		12
3/16/06	0.8	96	1164	3043	181	232	334	43	243	208		11
<b>LRA</b>												
1/99	0.4		90	489	12	14	30	6	20	19	12	
12/1/99	7.7		1881	8846	223	288	623	146	438	408	276	
1/01	4.4		950	5992	144	182	302	77	243	261	141	
3/02	4.5	247		860	7273	122	195	283	68	195	270	147
1/03	3.9			691	4170	94	167	210	45	157	210	120

can be summarized as follows  $C(t) = C_{ss}(1 - e^{-t/R}) + C(t=0)e^{-t/R}$  where  $C(t)$  is the concentration of an element at time  $t$ ,  $C_{ss}$  is the steady state concentration for a given input flux  $S_{in}$ ,  $C(t=0)$  is the initial element concentration at  $t=0$ ,  $R$  is the residence time of the element and  $t$  is time. The steady state concentration can be phrased as  $C_{ss} = (S_{in} R) / V$ . The goal of the model presented here is to derive variations in the volcanic element fluxes over time from the variations in the observed lake water compositions. I initially developed a model for the gradual contamination of Lake Cavihue over time, using a time step of one month and expressions for evolution towards steady state, with a change in input fluxes around the time that they were measured. These input fluxes were measured at yearly intervals, which introduces uncertainty because we do not know how representative they are. The residence time of water and the elemental residence times were estimated above, and are most likely similar because of the small evaporation to water input ratio. The steady state concentrations of conservative elements can be calculated from the input fluxes and element residence time. Potential errors that propagate through the calculations are the error in the measurements of the water fluxes and water compositions (see discussion in Guala-Valverde, 2005; Varekamp, 2005 and a more general discussion in Rimmer et al., 2006a,b), variations in lake volume and input/output water fluxes. I initially used expressions for a lake that is 6 months of the year stratified followed by 6 months of holomixis, which may approach the seasonal mixing behavior of Lake Cavihue (thermocline taken at 35 m depth).

An initial lake calibration model was obtained from the Cl analyses (Fig. 9a), which have a good precision on the IC (about +4% precision) and Cl behaves most likely conservative. The Cl models (small open triangles and dots) and analytical data show an increase in Cl concentrations from 1997 to early 1999 at an almost constant input flux, which is a non-steady state effect at that time: the steady state concentration for that input flux (107 ppm Cl at a residence time of 42 months) had not yet been reached. The Cl input flux dropped slightly during 1999, but then increased again during the eruption. The Cl flux must have dropped off very steeply after the eruption, creating declining Cl concentrations, but the flux recovered in 2002 and 2003. The mean lake Cl concentration varied from 80 to 100 ppm in 1997–2000, to return in 2003 back to about 75 ppm, then a slightly higher concentration in 2004 with a more dilute lake in 2006. Simulations for a stratified model (dots) and for a fully mixed model (triangles) using a residence time of 42 months (3.5 years) are shown in Fig. 9a. The results of a model using a 2.6-year water residence time (Rapacioli, 1985) are also shown for a fully mixed scenario, and these



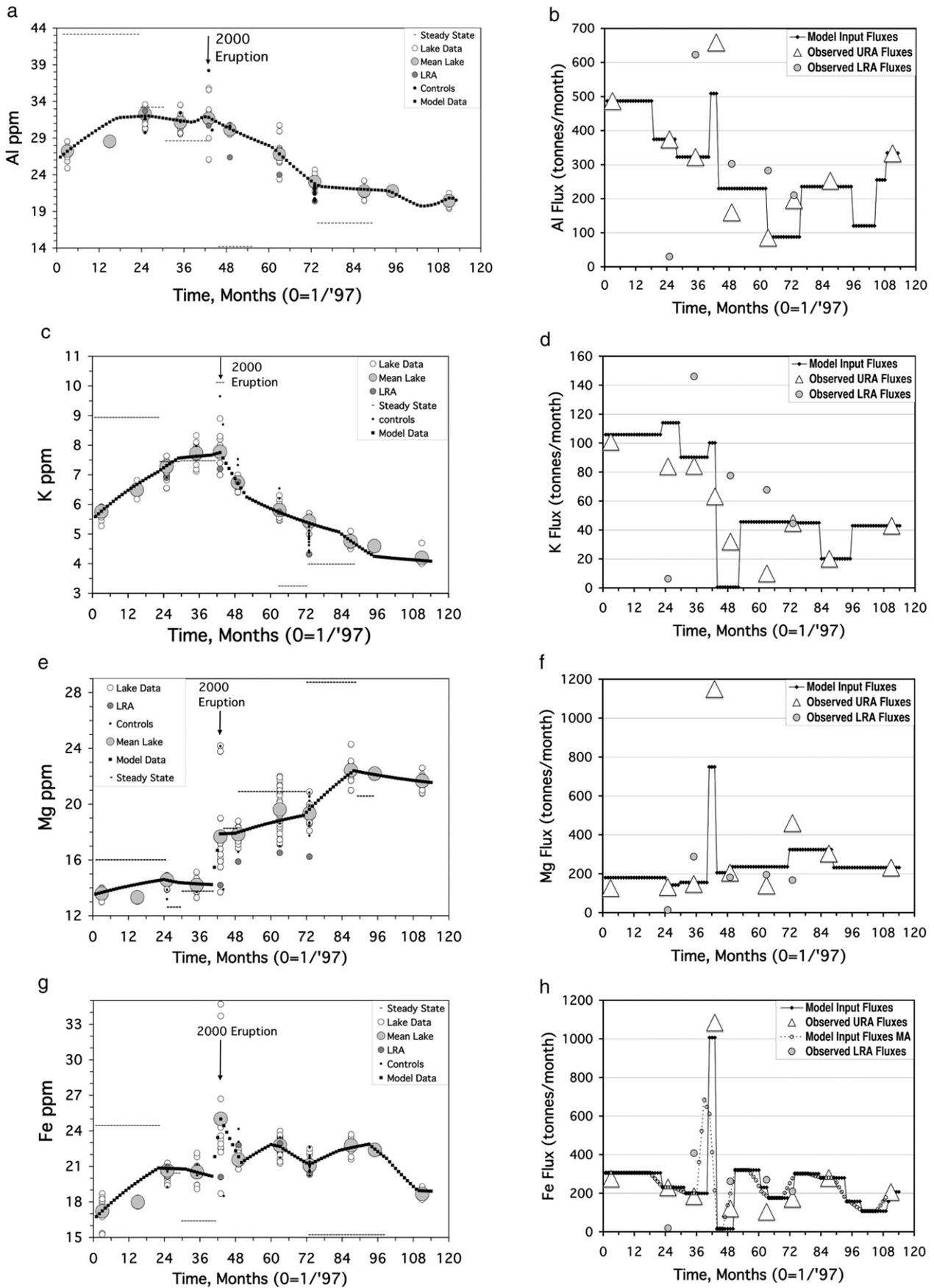
underestimate the observed concentrations. The 3.5-year residence time is slightly shorter than the 4 years estimated in Varekamp (2003), using fluxes and concentrations for Mg for the period 1997–2000, but is compatible with the modeling of the water flux data as shown in Fig. 3. The Cl model uses the measured input fluxes for the years 1997, 1999, 2000, and 2001. Similar runs were made for all other major elements and a best-fit residence time of 42 months (3.5 years) was adopted, assuming conservative behavior. From these initial runs it followed that the two-box model had only minor differences from the fully mixed model. I then applied a data inversion using the lake water data to constrain the best-fit fluxes and their variations over time with the 42 month residence time. This was accomplished with forward trial and error modeling until a satisfactory fit was obtained between input fluxes and mean lake water composition, using a complete mixing linear model, with constant lake volume, and the concentration in the outflow equals the mean lake concentration. The volcanic input from the URA was considered as the only element input source. The results are shown in pairs of figures (analytical data with model results and a comparison of model fluxes with observed fluxes) for some VE and RFE (Figs. 9 and 10). The element export fluxes of the LRA are also indicated on the graphs where available, and show that instantaneous true steady state is rare. The LRA element output fluxes are largely a function of the lake level, which controls the LRA outflow discharge rate. Nonetheless, the input and export fluxes are of the same order, indicating the dynamic equilibrium between inputs and outputs of the lake, with most likely an average steady state for water over an annual period.

The VE fluxes increased by a factor of 2 (Cl, F) to 3 (S) during the 2000 eruptive period and then fell strongly in 2001 to very low levels (~20% of the pre-eruptive fluxes, with S showing the largest drop). During 2002–2003 the volcanogenic element fluxes increased again to just below pre-eruptive levels, and F and Cl fluxes show a slight peak in 2004.

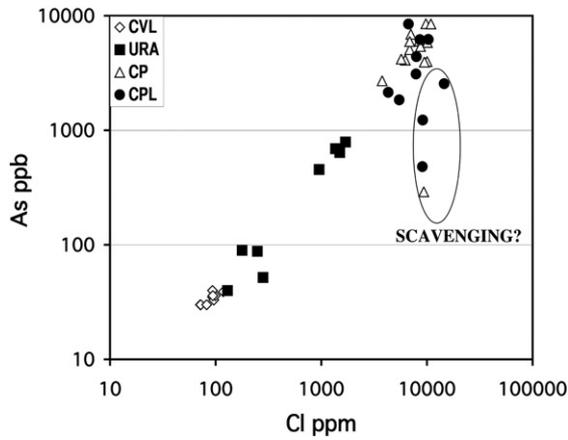
The time trends for the RFE concentrations in the lake and derived model fluxes (Fig. 10) show two groups of elements: all element concentrations (except K) increase during the 2000 eruption, but Al, Fe and K concentrations drop steeply after the eruption. The Mg concentrations increased after the eruption, the Fe fluxes increased again after 2001, whereas Ca and Na concentrations remained roughly constant. The RFE fluxes increased by a factor 2–4 during the eruption, except for K whose flux remained similar or even dropped during the eruptive period. The fluxes of Fe and K dropped to very low levels after the eruption, to recover to pre-eruptive levels afterwards (Fe) or remaining low for the next few years (K). The fluxes of Ca, Mg and Na fell to roughly pre-eruptive levels after the eruption. The only element that showed steadily increasing fluxes for the 4-year post-eruptive period is Mg. All the RFE fluxes show a slight increase during 2004, creating a maximum in lake water concentrations that is however below that of 2000. The silica fluxes are very modest for a major RFE (Table 3), and silica only builds up in the lake waters to about 12–17 ppm Si.

The agreement between model fluxes and observed fluxes is very good for most elements over the 9-year period, with some exceptions. Fluxes measured during the eruptive period were mostly equal or smaller than the mean model input fluxes. The 2000 fluxes were measured after the eruption had already started, and possibly the

**Fig. 9.** Time trends in Lake Caviahué for the volcanogenic elements, with model fluxes and observed fluxes. Annual lake water data (small open circles), annual mean lake water data (filled large circles), model data using the observed element fluxes for a fully mixed lake (small open triangles), model data for two-box lake (small filled circles), and best-fit model data (small filled squares). Steady state concentrations for the best-fit model fluxes are given as dashed lines. The time scale (in months) starts at January 1997 as month 1 and March 2006 is month 111 (last data point). a. Time–Cl trend with all model and observational data. The thin dashed line shows the model results for observed fluxes for a 2.6 years residence time. The comparison between model and observed fluxes for a residence time of 3.5 years is close except for 2006, which shows an unusually high Cl flux value. b. Time–SO<sub>4</sub> trend with best-fit model data with a residence time of 3.5 years; observed and model fluxes show good overall agreement.



**Fig. 10.** Time–element trends for RFE, with observed versus model flux data graphs. The Al and K concentrations strongly decreased after the eruption, whereas the Mg and Fe concentrations show an increase. Agreement between observed and model fluxes is shown for each element, with the closest agreement for the Fe fluxes. A moving average for the model Fe fluxes is shown as well, simulating the observed data quite closely.

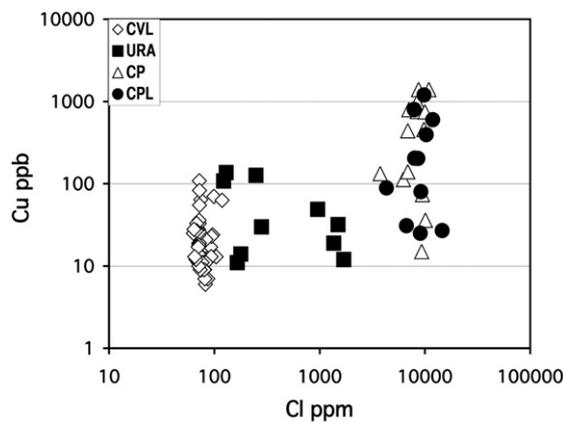


**Fig. 11.** Chloride–As relations in the Copahue–Caviahue fluids. Arsenic behaves conservatively from the very concentrated spring fluids to the rather dilute Lake Caviahue waters. Only 3 water samples of the crater lake and 1 hot spring sample show evidence for As loss, probably through precipitation and/or adsorption. CP: El Vertedero hot spring, CPL: Copahue crater lake, CVL: Lake Caviahue, URA: Upper Rio Agrio.

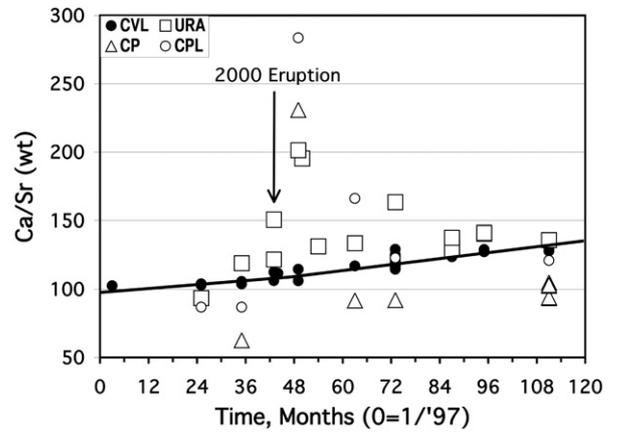
largest fluxes occurred just prior to or during the early eruptive events (Varekamp et al., 2001; Varekamp, 2003). The models cannot distinguish between the exact period of increased fluxes prior to the eruption and the magnitude of the flux, but using the observed Fe and Mg fluxes in 2000 provides an ~8 week period of enhanced input fluxes prior to the eruption. Enhanced element fluxes in 2003–2004 show up in the models and observed data, and indicate a more intense element discharge from the volcano at that time. In summary, most elements, including the conservative elements Cl and F, had constant or slightly decreasing fluxes prior to 2000, saw a strong flux increase during the eruption, followed directly thereafter by an almost complete shutoff of the hydrothermal system, only to recover in early 2002. From 2003 on and in 2004, the fluxes increased again and Lake Caviahue became slightly more concentrated and acidic, to become much more dilute again in 2006.

**7. Trace element trends and concentrations**

The trace elements Mn, P, Sr, Sc, Ti, V, Ni, Cu, Zn, Co, Cr, Y, Ba, B and As show various trends with time and depth. Some trace elements show similar behavior to one of the major elements, such as Mn behaves very much like Mg, Al correlates with Ti, and K correlates closely with P (see Pedrozo et al., 2008–this issue, for a detailed



**Fig. 12.** Chloride–Cu relations in the Copahue–Caviahue fluids. The Cu concentrations do not behave conservatively and are most likely scavenged by particles (see Parker et al., this issue). CP: El Vertedero hot spring, CPL: Copahue crater lake, CVL: Lake Caviahue, URA: Upper Rio Agrio.



**Fig. 13.** Time–Ca/Sr trend in Lake Caviahue waters and its feeding sources. The Ca/Sr values have risen from ~100 to 130 over the last 9 years. The Ca/Sr values in the feeding sources tend to be higher than the lake value, which may be a non-steady state effect or the result of Ca-sulfate precipitation along the way in the URA. The Ca/Sr values in the crater lake tend to be low, suggesting precipitation of a Ca-sulfate phase. CP: El Vertedero hot spring, CPL: Copahue crater lake, CVL: Lake Caviahue, URA: Upper Rio Agrio.

discussion of P behavior). These correlations largely indicate that these element pairs co-vary in the volcano effluents, behave conservatively throughout the watershed and in the lake water column, and thus follow similar compositional trends over time in Lake Caviahue. The toxic element As occurs at levels well above the WHO drinking-water standard (WHO, 1996) in URA waters (450–800 ppb) and at ~35 ppb in Lake Caviahue. The As and Cl concentrations correlate positively, suggesting close to conservative behavior from spring source to Lake Caviahue. A few crater lake and one hot spring sample suggest that As loss through co-precipitation or particle reactions may have occurred (Fig. 11). The behavior of the heavy metals Cu, Zn, Pb, Cr, Co, and Ni is much less predictable, with a wide range of possible concentrations at a given Cl level (Fig. 12). The metals also show little correlation amongst themselves. Complex particle–solute interactions probably occur (Parker et al., 2008–this issue).

The Ca/Sr was at ~100 prior to the eruption and increased to ~130 during the 9-year period (Fig. 13). The URA and CP input fluids had higher Ca/Sr during and after the eruption. The lack of a direct correlation of Ca/Sr between the URA and CVL waters is simply a non-steady state effect, but the changes in Ca/Sr over time in CP and URA samples reflects changes in ongoing water rock interaction inside the volcano or precipitation of secondary phases in the mountain or along the river flowpath.

**8. Discussion**

Lake Caviahue is continuously acidified through inputs of volcanic effluents. The pH has varied from 2.1 to 2.7 over the 9-year study period; the lake became less concentrated and less acidic after the 2000 eruption, to become slightly more acidic again in the years 2003–2004, and then more dilute again in 2006. The mean residence time that provides the best fit for the majority of the model element fluxes and concentration data is about 3.5 years.

The lake does not show strong compositional stratification although thermal stratification is common in austral summer and fall. Mixing driven by the fierce Patagonian winds that occur almost daily may homogenize part of the lake while the thermal stratification is restored much more rapidly than a chemical stratification. More closely spaced sampling intervals are needed to determine the temporal mixing properties of the lake. The northern and southern arms had only small compositional differences, which is somewhat puzzling because the URA tends to discharge more to the northern arm than to the southern arm. Again, strong winds may set up surface currents that mix the two arms on a regular basis. The lake displayed significant secular trends in composition over the 9-year sampling period, which are related to the

evolution towards steady state of the system and variations in the magnitude and composition of the volcanic inputs.

Two groups of elements are distinguished based on the secular element trends in Lake Caviahue waters:

- (1) The F, Cl, SO<sub>4</sub>, H, Al, and K concentrations show an increase between 1997 and 2000, a spike during the eruptive period (except K), followed by a strong decrease in 2001, with a slight increase in 2003–2004 followed by a decrease in 2006.
- (2) The elements Mg, Fe, Ca and Na show an increase between 1997 and 2000, a strong spike during the 2000 eruptive period, a variable drop for Fe, Ca and Na, but high input fluxes were maintained after 2001, leading to elevated concentrations in the lake waters in 2003–2006.

Our flux measurements indicate that the element fluxes all increased just prior to and during the eruptive period (with the exception of K), a result of increased concentrations of the RFE elements and enhanced flow of the volcanic springs (Varekamp et al., 2001). The deposition of ash by airfall into the lake during the eruption may have led to the dissolution of adsorbed elements on the ash, creating another element source. The release of adsorbed elements from ash that fell in the watershed may also have contributed to the enhanced element fluxes just after the eruption (Kringel, personal comm.). The data suggest a very sharp drop in element loading in 2001, indicating that the element release from the freshly fallen ash cannot have been a major process in the development of the lake water composition at that time. The strong drop in flux values just after the eruption stems from a decrease in element concentrations in the spring fluids and/or a decrease in spring flow rate. The elements K, Al, Fe and S show steep declines in fluxes just after the eruption, suggesting that a decrease in spring flow rate cannot be the only factor. Mineral saturation modeling of the Copahue hot spring fluids suggests that prior to the eruption the main saturated minerals were anhydrite and silica, whereas during and directly after the eruption the fluids were also saturated in alunite and K-jarosite (Varekamp et al., 2004). These minerals retain K, Al, Fe and S in the hydrothermal system, depleting these elements in the fluids. The river bed just downstream from the hot springs became coated with hematite, and gypsum and jarosite were detected in the river bed (Varekamp, 2004). The drop in the Cl flux after the eruption suggests that apart from a decrease in RFE concentrations of the system, the spring flow rate also decreased, indicating that the volcano–hydrothermal system had a lower permeability, probably a result of the increased rate of mineral precipitation. Over time, the permeability is possibly restored as a result of cooling (shrinkage), rock dissolution and possibly seismic fracturing of the system, and the element fluxes increased again. The higher fluxes of 2003–2004 suggest that either seismic fracturing occurred inside the hydrothermal system, creating fresh rock surfaces for water rock interaction, or a small magmatic intrusion occurred that was too small to lead to an eruption. The temperature of the crater lake was also high in 2003 (Trunk and Bernard, 2008–this issue), suggesting activity in the underlying hydrothermal cell. This possibly magmatic activity translated into higher element fluxes into the URA and raised elemental lake water concentrations in Lake Caviahue in late 2003 and 2004.

Precipitation of anhydrite/gypsum in the hydrothermal reservoir influences the Ca/Sr in the exiting waters. The Ca/Sr values in Copahue rocks ranges between 80 and 100, whereas the Ca/Sr in Lake Caviahue waters ranged over time from 100–130, suggesting a Sr depletion (or Ca enrichment) in the system over time. Anhydrite precipitation would lower the fluid Ca/Sr values. If a Sr-rich phase was precipitating from the fluids during the eruption and afterwards, the Ca/Sr would rise (as observed) but no such a phase has been indicated by saturation modeling of CP spring fluids. Dissolution of old hydrothermal anhydrite may explain the data, but this needs further study.

The S/Cl ratio in the Copahue fluids dropped by almost 50% in the years following the 2000 eruption (Fig. 14), which is caused to some

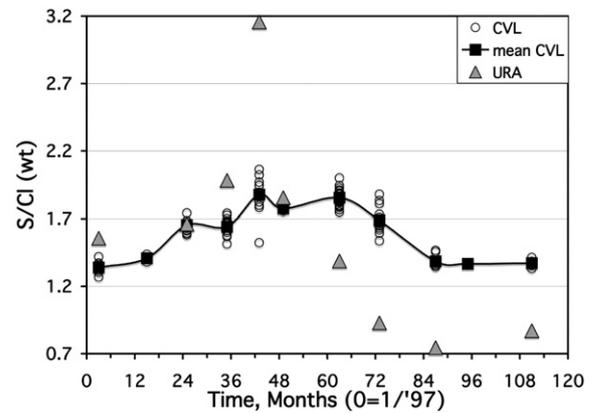


Fig. 14. S/Cl values in Lake Caviahue and URA waters. The ratio peaks during the eruption and then decreases. Note that the URA signal leads the CVL value.

degree by retention of anhydrite and alunite–jarosite. It may also be caused by the degassing of a residual batch of magma that had gases with a smaller S/Cl value than those from prior to and during the eruption (e.g., Symonds et al., 1994). The mean S/Cl value in Lake Caviahue water varied over the 9-year period from 1.34 in 1997 to 1.88 during the 2000 eruption to decrease again to 1.37 in 2006. The S/Cl signal in Lake Caviahue waters lags that of samples taken at the same time in the URA because of the non-steady state effects. The rise in element concentrations from 1997 till the 2000 eruption at almost constant input rate indicates that the preceding period had smaller element fluxes than those observed in this study, suggesting that Copahue was slowly becoming active after a lengthy period of rest.

The cumulative 9-year fluxes for S and Cl are 145,000 tons S and 83,000 tons Cl. The former is the equivalent of ~500 tonnes SO<sub>2</sub>/day that was fully scrubbed in the hydrothermal system (Symonds et al., 2001). The 9-year cumulative Mg flux is about 24,000 tons, which can be obtained through the congruent dissolution of ~40,000 m<sup>3</sup> of fresh rock per year. Of this dissolved rock, about half is retained as hydrothermal silica in the system, a fraction of space created by the rock removal is taken up by anhydrite, and after the eruption alunite–jarosite was retained. In addition, liquid elemental sulfur may occupy the pore spaces of the reservoir (Varekamp et al., 2001).

The average annual minor and trace element fluxes from this system are substantial as well: 1450 tonnes F, 6 tonnes As as well as 2 tonnes Li. Although large fluxes for a small watershed like the Rio Agrio, these values are insignificant when considering the global pollution fluxes of these toxic elements. If we assume that ~100 active volcanoes in the world have similar acid hydrothermal systems as Copahue (Varekamp et al., 2000), we estimate the global As flux from such hydrothermal volcanic sources at ~600–1000 tons As/year. The global input of arsenic to soils by human activities was estimated to be 52,000–112,000 tons per year in the 1980s (Nriagu and Pacyna, 1988).

## 9. Conclusions

Lake Caviahue is acidified by volcanic fluids creating a pH between 2.1 and 2.7 in the lake waters for more than 9 years. The buffering capacity of the local rocks is very small and little alkalinity is generated inside the lake through local reactions with rock or sediment. The major element composition of the lake showed a trend of increasing concentrations from 1997 to 1999, followed by a sharp increase just prior to and during the eruption, followed by a strong drop in concentrations of Al, K, Fe, SO<sub>4</sub>, Cl, and F, but increasing concentrations of Na, Mg and Ca. The volcanic springs that feed the URA and the lake provide both an essential nutrient (P) to the lake as well as several toxins, including As.

The water balance and earlier modeling attempts indicate that a mean residence time of 3.5 years describes the system adequately.

Inversion of the secular element data from the lake using a calibrated lake model provided information on variations in element input fluxes over time, and these estimates showed overall good agreement with observed flux measurements. Variations in the composition of the URA over time are the result of fluctuations in the composition and flow rates of the feeding volcanic springs, the degree of dilution with glacial melt water and contributions of elements from the tributary rivers of the URA. The variations in elemental output of the volcano are possibly related to seismic activity in the hydrothermal system that creates new fracture permeability which leads to enhanced flow rates of the hot springs and new surfaces for acid attack. The increased element fluxes may have signaled the arrival of an “eruption that never was”, and magmatic intrusion may have taken place without any eruptive activity. The river water composition can be used as a potential indicator for pending volcanic activity, and if future eruptions follow a similar pattern as the 2000 eruptions, then an overall increase in element fluxes with higher ratios between some of the rock forming elements and Cl would be an initial indicator prior to a forthcoming eruption. The Mg concentration in the spring fluids seems to be a good indicator for enhanced water rock interaction in the system as encountered during intrusion of new magma, whereas the K concentrations appear to drop sharply as a result of alunite/jarosite precipitation. Monitoring changes in the S/Cl, Mg/Cl and Mg/K values in the URA near the bridge in Caviahue on a weekly basis may thus provide a crude first order volcanic risk indicator for the village and sudden changes may indicate new activity of the mountain. Over the 9-year period, the Mg/Cl value in the lake increased from 0.1 to 0.3, but the Mg/Cl value in the URA started to drop again in 2006, which will be followed by a drop in the value in the lake over time. Establishment of a flow gauge with some specific ion probes and a data collection station would be a more professional approach to volcano monitoring that ultimately may be of benefit to the local population. Monitoring the composition of Lake Caviahue does not generate predictive capabilities on the short term, because of the delay of the appearance of volcanic signals in the lake compared to the source signals on the mountain.

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## References

- Beamud, S.G., Diaz, M.M., Pedrozo, F.L., 2007. Summer phytoplankton composition and nitrogen limitation of the deep, naturally acidic (pH=2.2) Lake Caviahue, Patagonia, Argentina. *Limnologia* 37, 37–48.
- Bekessy, S.A., Allnutt, T.R., Premoli, A.C., Lara, A., Ennos, R.A., Burgman, M.A., Cortes, M., Newton, A.C., 2002. Genetic variation in the vulnerable and endemic Monkey Puzzle tree, detected using RAPDs. *Heredity* 88, 243–249.
- Bermudez, A., Delpino, D., 1995. Mapa de los peligros potenciales en el área del Volcán Copahue – sector Argentino. Volcanic Hazard map published by the Geological Survey of the Province of Neuquen, Argentina.
- Casertano, L., 1964. Some reflections on the fumarolic manifestations of the Los Copahues crater. *Bulletin of Volcanology* 27, 197–215.
- Christenson, B.W., 2000. Geochemistry of fluids associated with the 1995–1996 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic hydrothermal system. *J. Volcanology and Geothermal Research* 97, 1–30.
- Collier, R., Dymond, J., McManus, J., Lupton, J., 1990. Chemical and physical properties of the water column at crater lake, OR. In: Drake, E.T., Larson, G.L., Dymond, J., Collier, R. (Eds.), *Crater Lake: an Ecosystem Study*. AAAS-Pacific Division, pp. 69–80.
- Delmelle, P., Bernard, A., 2000a. Volcanic lakes. *Encyclopedia of Volcanology*. Academic Press, pp. 877–896.
- Delmelle, P., Bernard, A., 2000b. Downstream composition changes of acidic volcanic waters discharged into the Banyupahit stream, Ijen caldera, Indonesia. *Journal of Volcanology and Geothermal Research* 97, 55–75.
- Delmelle, P., Bernard, A., Kusakabe, M., Fisher, T.P., Takano, B., 2000. Geochemistry of the magmatic hydrothermal system of Kawah Ijen volcano, east Java, Indonesia. *Journal of Volcanology and Geothermal Research* 97, 31–53.
- Delpino, D., Bermudez, A., 1993. La Actividad del Volcan Copahue durante 1992: Erupcion con emisiones de azufre piroclastico, Provincia del Neuquen, Argentina: XII Congreso Geologico Argentino y II Congreso de Exploracion de Hidrocarburos, Actas T., IV, pp. 292–301.
- Delpino, D., Bermudez, A., 1995. Eruptions of pyroclastic sulphur at crater lake of Copahue Volcano, Argentine: International Union of Geodesy and Geophysics. XXI General Assembly. Abstracts volume, p. 128.
- Delpino, D., Varekamp, J.C., Bermudez, A., 1997. Influencia de un sistema volcanico activo sobre un lago de origen glacial: Lago Caviahue, Neuquen, Argentina. *Proceedings of 7th International Conference on Lakes Conservation and Management*, Bariloche, Argentina, pp. 1–4.
- Delpino, D.H., Bermudez, A.M., 2002. La erupcion del volcan Copahue del ano 2000. Impacto social y al medio natural. Provincia del Neuquen, Argentina. *Actas del XV Congreso Geologico Argentino, El Calafate*, p. 6.
- Diaz, M.M., Pedrozo, F.L., Reynolds, C., Temporetti, P., 2007. Chemical composition and the nitrogen regulated trophic state of Patagonian lakes. *Limnologia* 37, 17–27.
- Evans, W.C., Kling, G.W., Tuttle, M.I., Tanyileke, G., White, L.d., 1993. Gas buildup in lake Nyos, Cameroon – the recharge process and its consequences. *Applied Geochemistry* 8, 207–221.
- Fehn, U., Snijder, G., Varekamp, J.C., 2002. Detection of recycled marine sediment components in crater lake fluids using <sup>129</sup>I. *Journal of Volcanology and Geothermal Research* 115, 451–460.
- Gammons, C.H., Wood, S.A., Pedrozo, F., Varekamp, J.C., Nelson, B., Shope, C.L., Baffico, G., 2005. Hydrogeochemistry and rare earth element behavior in a volcanically acidified watershed in Patagonia, Argentina. *Chemical Geology* 222, 249–267.
- Giggenbach, W.F., Glover, R.B., 1975. The use of chemical indicators in the surveillance of volcanic activity affecting the crater lake on Mt. Ruapehu, New Zealand. *Bulletin of Volcanology* 39, 70–81.
- Gomez, D., Smichowski, P., Polla, G., Ledesma, A., Resnizky, S., Rosa, S., 2002. Fractionation of elements by particle size of ashes ejected from Copahue Volcano, Argentina. *Journal of Environmental Monitoring* 4, 972–977.
- Guala-Valverde, J., 2005. Comment on “Lake contamination models”. *Journal of Limnology* 64 (2), 159–160.
- GVN, 2000a. Frequent Ash Explosions and Acidic Mudflows Starting on July 1. *Bulletin of Global Volcano Network*, vol. 25, p. 6.
- GVN, 2000b. Continued Ash Explosions and Tremor During August–October. *Bulletin of Global Volcano Network*, vol. 25, p. 9.
- Heikens, A., Sumarti, S., Van Bergen, M., Widianarko, B., Fokkert, L., van Leeuwen, K., Seinen, W., 2005. The impact of the hyperacid Ijen crater lake: risks of excess fluoride to human health. *Science of the Total Environment* 346, 56–69.
- Kling, G.W., Evans, W.C., Tanyileke, G., Kusakabe, M., Ohba, T., Yoshida, Y., Hell, J.V., 2005. Degassing Lakes Nyos and Monoun: defusing certain disaster. *Proceedings National Academy of Sciences* 102, 14185–14190.
- Koschorreck, M., Wendt-Potthoff, K., Scharf, B., Rchnow, H.H., 2008. Methanogenesis in the sediment of the acidic Lake Caviahue in Argentina. *Journal of Volcanology and Geothermal Research* 178, 197–204. doi:10.1016/j.jvolgeores.2008.06.017.
- Martinez, M., Fernandez, E., Valdes, J., Barboza, V., van der Laat, R., Duarte, E., Malavassi, E., Sandoval, L., Barquero, J., Marino, T., 2000. Chemical evolution and volcanic activity of the active crater lake of Poas volcano, Costa Rica, 1993–1997. *Journal of Volcanology and Geothermal Research* 97, 127–142.
- Martini, M., Bermudez, A., Delpino, D., Giannini, L., 1997. The Thermal Manifestations of Copahue Volcano Area, Neuquen, Argentina. VIII Congreso Geologico Chileno, vol. 1. Universidad Catolica del Norte, pp. 352–356.
- Mayr, C., Lu, A., Stichler, W., Trimborn, P., Ercolano, B., Oliva, G., Ohlendorf, C., Soto, J., Fey, M., Haberzettl, T., Janssen, S., Scha, F., Schleser, G.H., Wille, M., Zolitschka, 2007. Precipitation origin and evaporation of lakes in semi-arid Patagonia (Argentina) inferred from stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ). *Journal of Hydrology* 334, 53–63.
- Melnick, D., Folguera, A., Ramos, V.A., 2006. Structural control on arc volcanism: the Caviahue–Copahue complex, Central to Patagonian Andes transition (38S). *Journal of South American Earth Sciences* 22, 66–88.
- Naranjo, J.A., Polanco, E., 2004. The 2000 AD eruption of Copahue Volcano, Southern Andes. *Revista Geológica de Chile* 31 (2), 279–292.
- Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. *Nature* 333, 134–139.
- Ouimette, A.P., 2000. Hydrothermal processes at an active volcano, Copahue, Argentina. MA thesis, Wesleyan University, Middletown CT pp.220.
- Parker, S.R., Gammons, C.H., Pedrozo, F.L., Wood, S.A., 2008. Diel changes in metal concentrations in a geogenically acidic river: Rio Agrio, Argentina. *Journal of Volcanology and Geothermal Research* 178, 213–223. doi:10.1016/j.jvolgeores.2008.06.029.
- Pasternack, G.B., Varekamp, J.C., 1997. Volcanic lake systematics I. Physical constraints. *Bulletin of Volcanology* 58, 528–538.
- Pedrozo, F., Kelly, L., Diaz, M., Temporetti, P., Baffico, G., Kringel, R., Friesse, K., Mages, M., Geller, W., Woelfl, S., 2001. Water chemistry, plankton and trophic status of

- an Andean acidic lake of volcanic origin in Patagonia. *Hydrobiologia* 452, 129–137.
- Pedrozo, F.L., Temporetti, P.F., Beamud, G., Diaz, M.M., 2008. Volcanic nutrient inputs and trophic state of Lake Caviahue, Patagonia, Argentina. *Journal of Volcanology and Geothermal Research* 178, 205–212. doi:10.1016/j.jvolgeores.2008.06.018.
- Pesce, A., 1989. Evolucion volcano tectonica del complejo efusivo Copahue–Caviahue y su models geotermico preliminary. *Revista Asociacion Geologica Argentina* 44, 307–327.
- Rapacioli, R., 1985. Lake Caviahue and its basin. Tech. Report, EPAS Gov. Office, Province of Neuquen, Argentina, pp. 1–72.
- Rimmer, A., Eckert, W., Nishri, A., Agnon, Y., 2006a. Evaluating hypolimnetic diffusion parameters in thermally stratified lakes. *Limnology and Oceanography* 51 (4), 1906–1914.
- Rimmer, A., Boger, M., Aota, Y., Kumagai, M., 2006b. A lake as a natural integrator of linear processes: application to Lake Kinneret (Israel) and Lake Biwa (Japan). *Journal of Hydrology* 319, 163–175.
- Rimmer, A., Aota, Y., Kumagai, M., Eckert, W., 2005. Chemical stratification in thermally stratified lakes: a chloride mass balance model. *Limnology and Oceanography* 50, 147–157.
- Rowe Jr, G.L., Brantley, S.L., Fernandez, M., Fernandez, J.F., Borgia, A., Barquero, J., 1992a. Fluid–volcano interaction in an active stratovolcano: the crater lake system of Poas volcano, Costa Rica. *Journal of Volcanology and Geothermal Research* 49, 23–51.
- Rowe Jr, G.L., Ohsawa, S., Takano, B., Brantley, S.L., Fernandez, J.F., Barquero, J., 1992b. Using crater lake chemistry to predict volcanic activity at Poas volcano, Costa Rica. *Bulletin of Volcanology* 54, 494–503.
- Schmid, M., Halbwegs, M., Wehrli, B., Wüest, A., 2005. Weak mixing in Lake Kivu: new insights indicate increasing risk of uncontrolled gas eruption. *Geochemical Geophysical Geosystem* 6, Q07009. doi:10.1029/2004GC000892.
- Sriwana, T., van Bergen, M.J., Sumarti, S., de Hoog, J.C.M., van Os, B.J.H., Wahyuningih, R., Dam, M.A.C., 1998. Volcanogenic pollution by acid water discharges along Ciwidey River, West Java (Indonesia). *Journal of Geochemical Exploration* 62, 161–182.
- Sriwana, T., van Bergen, M.J., Varekamp, J.C., Sumarti, S., Takano, B., van Os, B.J.H., Leng, M.J., 2000. Geochemistry of the acid Kawah Putih lake, Patuha volcano, west Java, Indonesia. *Journal of Volcanology and Geothermal Research* 97, 77–104.
- Symonds, R.B., Rose, W.I., Bluth, G.J.S., Gerlach, T.M., 1994. Volcanic gas studies: methods, results and applications. *Reviews in Mineralogy* 30, 1–66.
- Symonds, R.B., Gerlach, T.M., Reed, M.H., 2001. Magmatic gas scrubbing: implications for volcano monitoring. *Journal of Volcanology and Geothermal Research* 108, 303–341.
- Takano, B., Ohsawa, S., Glover, R.B., 1994. Surveillance of Ruapehu crater lake, New Zealand, by aqueous polythionates. *Journal of Volcanology and Geothermal Research* 60, 29–57.
- Takano, B., Fazlullin, S.M., Delmelle, P., 2000. Analytical laboratory comparison of major and minor constituents in an active crater lake. *Journal of Volcanology and Geothermal Research* 97, 497–508.
- Trunk, L., Bernard, A., 2008. Investigating crater lake warming using ASTER thermal imagery: case studies at Ruapehu, Poás, Kawah Ijen, and Copahué Volcanoes. *Journal of Volcanology and Geothermal Research* 178, 259–270. doi:10.1016/j.jvolgeores.2008.06.020.
- Varekamp, J.C., 1988. Lake pollution modeling. *Journal of Geological Education* 36, 4–9.
- Varekamp, J.C., Pasternack, G.B., Rowe, G.L., 2000. Volcanic lake systematics II. Chemical constraints. *Journal of Volcanology and Geothermal Research* 97, 161–180.
- Varekamp, J.C., Ouimette, A., Herman, S., Delpino, D., Bermudez, A., 2001. The 1990–2000 eruptions of Copahue, Argentina: a ‘bee-hive volcano’ in turmoil. *Geology* 29, 1059–1062.
- Varekamp, J.C., 2003. Lake contamination models for evolution towards steady state. *Journal of Limnology* 62 (suppl.1), 67–72.
- Varekamp, J.C., 2004. Copahue Volcano: a modern terrestrial analog for the Opportunity landing site. *Eos* 85 (#41), 401–407.
- Varekamp, J.C., Ouimette, A., Kreulen, R., 2004. In: Wanty, R.B., Seall II, R.R. (Eds.), *The Magmato-hydrothermal System of Copahue Volcano, Argentina*. Proceedings of the 11th Water Rock Interaction Symposium, vol. 1. Balkema Publishers, Leiden, pp. 215–218.
- Varekamp, J.C., 2005. Reply to comment by Jorge Guala-Valverde on: “Lake contamination models”. *Journal of Limnology* 64 (2), 159–160.
- Varekamp, J.C., deMoor, J.M., Merrill, M.D., Colvin, A.S., Goss, A.R., Vroon, P.Z., Hilton, D.R., 2006. The geochemistry and isotopic characteristics of the Caviahue Copahue Volcanic Complex, Province of Neuquen, Argentina. *GSA Special Paper* 407, 317–342.
- Wendt-Potthoff, K., Koschorreck, M., 2002. Functional groups and activities of bacteria in a highly acidic volcanic mountain stream and lake in Patagonia, Argentina. *Microbial Ecology* 43, 92–106. doi:10.1007/s00248-001-1030-8.
- Wetzel, R.G., 1983. *Limnology*. Saunders College Publishing, p. 203.
- WHO, 1996. *Guidelines for Drinking-water Quality*, 2e edition. Geneva, Switzerland.