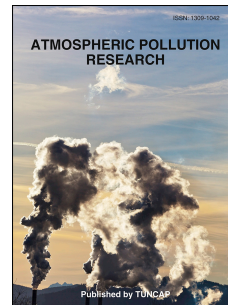


# Journal Pre-proof

Mercury in a geothermal and volcanic area in Patagonia, southern South America

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Author contribution to the manuscript

**Soledad Perez Catán:** Conceptualization, Formal analysis, Investigation, Writing - Original Draft and Editing

**Débora Bubach María Inés Messuti and María Angélica Arribére:** Resources; Investigation and Writing - Review

**Sergio Ribeiro Guevara:** Funding acquisition

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**Mercury in a geothermal and volcanic area in Patagonia, southern South America**

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**Abstract:**

Mercury and heavy metal contents are monitored using lichens as a tool for evaluation of air pollution. Lichens allow the identification of zones with anthropic impact, pollution hotspots and natural sources of contamination like volcanic emissions. The concentration of mercury (Hg) semivolatiles and rare-earth elements (REEs) were measured in our case in fruticose lichen thalli and soils collected in an active volcanic area: the Copahue-Caviahue Volcanic Complex, in northern Patagonia, South America. The present research focus on Hg-release patterns and its association to elements such as sulphur (S) and bromine (Br). In order to discriminate the particulate from the gaseous forms the concentration ratios of elements to magnesium (Mg) were computed. The Hg vs. Br concentration linear regression, together with the Hg normalised concentration vs. volcano distance, suggest that Hg from volcanic origin may be oxidised changing to reactive forms in the ash plume. Total mercury concentration in fruticose lichens ( $0.207\text{-}0.331\ \mu\text{g g}^{-1}$ ) in Copahue-Caviahue volcanic area were higher than those from several other volcanic areas in South America, USA and Italy ( $0.010\text{-}0.290\ \mu\text{g g}^{-1}$ ). Nevertheless, the consequent deposition has not generated a net contamination in soils.

**Keywords:** Biomonitoring, Fruticose lichen, Gaseous elemental mercury, Remote region, Volcanic mercury

**1. Introduction**

Gaseous elemental mercury,  $\text{Hg}^0$  (GEM), is the most frequent chemical form in the atmosphere (>95%). Other chemical mercury (Hg) forms (<5%) are rapidly deposited by wet and dry deposition, including reactive gaseous compounds and water soluble, as for example  $\text{HgCl}_2$ ,  $\text{HgO}$ ,  $\text{Hg}(\text{OH})_2$ ,  $\text{HgBr}_2$ ,  $\text{CH}_3\text{-}$  and  $\text{C}_2\text{H}_6\text{-}$  (Amos et al., 2012).

Atmospheric Hg monitoring based on direct instrumental measurements has been performed in several studies (Higuera et al., 2005; Lopez Berdonces et al., 2017). These instrumental data are extremely variable because volatilization rates of GEM from the surfaces depend on several factors, such as light, temperature, soil moisture, vegetation cover, barometric pressure, cloud

coverage and wind (Bargagli, 2016). In terrestrial ecosystems, Hg deposition assessment methods using lichens are less expensive compared to instrumental. Lichens have ideal accumulative characteristics due to its slow-growing rate and long life, reflecting atmospheric Hg loads and integrated deposition rates (Zvěřina et al., 2018). This allows to have access to mercury hotspots with a limited amount of samples, and to sites with a suitable spatial distribution (Lodenius, 2013; Nimis et al., 2000).

According to Lopez Berdonces et al. (2017), lichens are exposed to atmospheric deposition, so they detect all the chemical forms of Hg (soluble, particulate and gaseous). The average concentration of Hg in mosses and fruticose lichens samples collected at different distances from active volcanoes and geothermal sources has been rather low compared with that of sites impacted by anthropic activity (Bargagli, 2016). Historical records obtained from measurements made in ice cores, lake sediments and peat, in remote locations and at high altitudes, suggested a preindustrial background Hg concentration of 3–4 ng L<sup>-1</sup> (from ice-core record) without influence from short-term emissions (< 2 years) of volcanic activity (Schuster et al., 2002). Mercury emissions from active volcanoes are the main natural source of direct release into the atmosphere (Bagnato et al., 2014; Nriagu and Becker, 2003). Pyle and Mather (2003) estimated the average volcanic Hg emission based on data from active volcanoes and this value represents 20–40% of natural emissions in the whole world. The temporal variation of Hg releases as gasses or ash during the stages of an active volcano has not been well recorded until present, and large uncertainties persist, especially regarding South America volcanoes (Nriagu and Becker, 2003; Slemr et al., 2015).

The Andean Volcanic Belt is a major volcanic belt along the Andean cordillera in South America; the South Volcanic Zone (SVZ) extends over 1,400 km in Central Chile's Andes at a latitude of circa 33°S to 46°S. This is an active volcanic region with historically high eruptive frequency and a high impact over Patagonia. Limited research has been performed on the environmental impact associated with elements released from volcanic activity in Northern Patagonian Andes (Paez et al., 2017; Perez Catán et al., 2016; Petrinovic et al., 2014), particularly of semivolatile elements (Bubach et al., 2012).

The Copahue is a stratovolcano, which belongs to the SVZ. It presents an acid lake inside the crater. In this lake, magma degasses and the permanent emission of smoke increase the release of volatile elements, such as halides and Hg, into waters of the hydrothermal system and into the atmosphere (Heinrich et al., 1999). Copahue volcano eruptive record dates back to the seventeenth century with events considered of low magnitude; strong explosions accompanied by ash and gas emissions occurred in the 1950's, 1992, and between 2012 and 2017.

Lichen thalli analysis represents a valuable opportunity to study Hg deposition in areas where volcanic activity is manifested, such as geothermal fields and places with both pyroclastic and lava eruptions (Bargagli, 2016). The constant Hg releases from Copahue volcano distribute spatially according to meteorological parameters. The mercury deposition on terrestrial ecosystems occurs together with other semivolatile elements, such as sulphur (S), arsenic (As), selenium (Se) and Br. In this work, we will analyse Hg deposition patterns and its impact to the environment compared to that of other elements, and the distance to the volcanic emission sources.

## **2. Materials and methods**

Lichen thalli and soil samples were collected in the same sites, shown in Figure 1. The study area is located at the east of the Patagonian Andes, in Copahue-Caviahue Provincial Park, Neuquén province, Argentina ( $37^{\circ} 47' - 37^{\circ} 55' \text{ S}$  and  $70^{\circ} 55' - 71^{\circ} 10' \text{ W}$ ). The area is characterised by a particular volcanic geomorphology and a glacial and fluvial landscape. The most important water sources are the Agrio river, which flows into and out of Caviahue lake, and the Dulce, Trolope and Hualcupén streams.

The greatest eruption events occurred in 1992, 2000 and 2012 (see Figure 1), and the permanent gas emission at the crater and hot springs were taken into account in the selection of the sampling sites. Eleven sites located between 6.5 to 18 km from the volcano crater in the Copahue-Caviahue volcanic area (CCv) were sampled on March 2017. These sites were chosen in order to evaluate the distribution patterns of volcanic products according to the predominant westerly winds.

Lichens sampling was done by random walk and fruticose species above 0.60 to 1m were collected when they were present. *Usnea* and/or *Protousnea* genera were represented in all sites except in Upper Río Agrio (RA) area, where lichens were absent. In each sampling site, one sample ensemble, representative of at least five shallow soils, was taken around the lichen area. The collection of lichen (entire thalli, n=5-10) and soil samples was made using latex gloves, titanium devices or plastic tools, and sterile polyethylene bags. Substrate remains were removed from the thalli under dissecting stereomicroscope at room temperature (22°C). Then, they were rinsed three times with the American Society for Testing and Materials (ASTM) grade 1 water in order to eliminate the abundant superficial dust (Garty and Garty-Spitz, 2015) and to be dried in a laminar flow hood and lyophilised. Pooled samples of 5-10 dried lichen thalli of each site were thinly cut and homogenised to a fine powder. Surface soil samples, taken at 2-3 cm depth with plastic spoons, were placed in plastic jars with screw caps. All the samples were kept frozen at -20°C until freeze drying, and then were sieved with 125 µm mesh before the analysis.

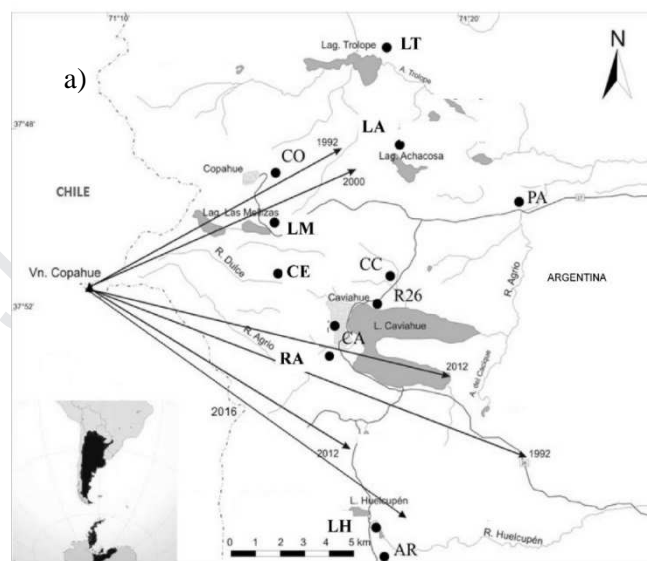


Figure 1: Study area of the Copahue-Caviahue Volcanic Complex (CCv), Neuquén, Argentina. Sampling sites of lichens and soils: Copahue town (CO); Laguna Las Mellizas (LM); Laguna Trolope (LT); Laguna Achacosa (LA); Puente del Agrio (PA); Cascada Escondida (CE); Caviahue town (CA); Camping Caviahue (CC); Ruta Provincial N°26 (R26); Laguna Huelcupén (LH) and Arroyo Las Lecheras (AR).

Lichen and soil samples were analysed for their elemental composition by Instrumental Neutron Activation Analysis (INAA). Aliquots of lichen samples ranging in mass from 100 to 150 mg were put in quartz ampoules and sealed for analysis, whereas aliquots of soil samples, ranging in 100 mg, were placed in plastic vials. The samples were irradiated in the RA-6 nuclear reactor (MTR type, 1 MW thermal power) at Centro Atómico Bariloche. Two irradiations were performed for each sample. The first one consisted of a short-term irradiation in a predominantly thermal neutron flux ( $2 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ ) during 3 to 5 minutes for the lichen samples, and during 1 minute for soil samples. Then, gamma-ray spectra were collected at different decay times. A second irradiation was performed in the reactor core (thermal, epithermal, and fast neutron fluxes of  $1.5 \times 10^{13}$ ,  $8 \times 10^{11}$ , and  $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ , respectively) during 20 hours for lichen samples, and during 6 hours for soil samples. After irradiation, soils were changed to unirradiated vials before counting to avoid the interference of vial impurities, and several gamma-ray spectra were collected at different decay times. The gamma-ray spectra were collected with coaxial HPGe detectors (10 % and 30 % relative efficiency and 1.8 keV resolution at 1.33 MeV) and a 4096-channel analyser. To determine the elemental concentration, the absolute parametric method was used. Thermal and epithermal neutron fluxes were measured for long-term irradiation by the  $(n, \gamma)$  reactions of the pair Zn–Au, using high purity wires of pure Zn and 0.100 % Au–Al alloy. As for the short term irradiation, the thermal neutron fluxes were determined by the  $(n, \gamma)$  reaction of Mn, using high purity wires of a 80.2 % Mn–Cu alloy. Corrections for spectral interferences were performed when necessary. Analytical



errors were computed as the propagation of the uncertainties associated with the nuclear parameters, the efficiency of the gamma-ray detection system, the neutron flux determination, and the area of the specific emission considered. Several elements were determined: antimony (Sb), arsenic (As), barium (Ba), bromine (Br), caesium (Cs), cobalt (Co), Hg, selenium (Se), thorium (Th), uranium (U), and Zn; the essential calcium (Ca), iron (Fe), potassium (K), magnesium (Mg) and sodium (Na); the Rare Earth Elements (REE) cerium (Ce), europium (Eu), lanthanum (La), lutetium (Lu), neodymium (Nd), samarium (Sm), terbium (Tb), and ytterbium (Yb), and the trace elements hafnium (Hf), rubidium (Rb), scandium (Sc), strontium (Sr), and tantalum (Ta). The analytical quality control (QC) was checked with the results of analysing Reference Material IAEA lake sediment and NIST Buffalo River sediment (see Supplementary Materials, Table S1) and IAEA 336 Lichen Reference Material (Supplementary Materials, Table S2), which were processed together with the samples.

Sulphur contents were measured by LECO method (HF-100 Induction Furnaces model 777- 400 SN 675) in whole thalli (Mark et al., 1989).

To estimate the relative abundance of volatile species like Hg, S, Br and Se in the magmatic gas emissions and/or fumarole, the concentration of non-volatile elements, in this case Mg, was used (Allard et al., 2000; Kodamatani et al., 2018). Pearson's correlation among elements and distance to the crater was calculated in order to estimate the dispersion pattern. The statistical analyses were conducted using XLSTAT software (copyright 1995-2009 Addinsoft) and the significance level considered in statistical tests was  $\alpha \leq 0.05$ .

### **3. Results**

#### **3.1. Soils**

Figure 2 shows multi-elemental diagrams normalised to the primitive mantle (average values; McDonough and Sun, 1995). The element concentration diagrams ordered around incompatibility grade (White, 2013) are usually used to identify sources. The incompatibility of the element is defined when its partition coefficient is less than 1. In geochemistry, some

elements have difficulty moving within the mineral and will be concentrated in the melting phase of magma (liquid phase). Copahue volcanic ash, glass debris and other volcanic products of 2000 and 2012 eruptions taken from Daga et al. (2017) and soil samples of this work (see Figures 2a and 2b respectively) were compared to the same multi-elemental diagrams in order to determine the element sources that could affect terrestrial ecosystems.

Elemental concentration of soil samples from Copahue-Caviahue volcanic area (CCv) are shown on Table 1, Average values are given for sampling sites and the measured values together with the uncertainties of supplementary materials are shown on Table S3. Bromine, Hg, Se and S concentration showed a high coefficient of variation among sampling sites (CV >30; Table 1).

Copahue volcano distance does not correlate with the concentration of semivolatile elements in soils. The comparison of Hg contents in soils and lichens with distance to the volcano is shown in Figure 3.

Table 1: Elemental concentration expressed in  $\mu\text{g g}^{-1}$  dry weight of soil samples from Copahue-Caviahue region (average values among sampling sites)

	Average concentration	Standard deviation (SD)	Coefficient of variation (CV: (%))
Al ( $\times 10^{-4}$ )	8.88	0.47	5.3
As*	6.7	1.5	22
Ba	412	59	14
Br	9.14	3.43	38
Ca ( $\times 10^{-4}$ )	4.18	0.33	8.0
Cd	10.2	2.9	29
Ce	54.4	7.1	13
Co	24.2	3.9	16
Cr *	69	21	31
Cs	3.10	0.44	14
Eu ( $\times 10^3$ )	1.44	0.12	8.6
Fe ( $\times 10^{-4}$ )	2.62	0.27	11
Hf	5.26	0.99	19
Hg	0.37	0.16	43
K ( $\times 10^{-4}$ )	1.14	0.34	30
La	22.3	3.7	17
Lu ( $\times 10^3$ )	0.391	0.041	11
Mg ( $\times 10^{-4}$ )	2.42	0.34	14
Mn	1110	170	16
Na ( $\times 10^{-4}$ )	2.30	0.24	10
Ni*	35	11	31
Rb	47.4	9.9	21
Sb ( $\times 10^3$ )	0.296	0.059	20
Sc	23.4	2.2	9.3
Se	0.78	0.74	94
Sm	5.61	0.71	13
Sr	489	52	11
S	1140	155	31
Ta	0.44	0.10	21
Tb	0.77	0.10	13
Th	7.2	1.7	24
Ti ( $\times 10^{-4}$ )	0.767	0.085	11
U	1.99	0.52	26
V	196	25	13
Yb	5.99	0.52	8.7
Zn	102	11	11
Zr	204	39	19

\* AS, background levels in the lithosphere: 0.2 to 15  $\mu\text{g g}^{-1}$ ; Cr, Italian regulation: 150  $\mu\text{g g}^{-1}$ ; Ni: 1600  $\mu\text{g g}^{-1}$

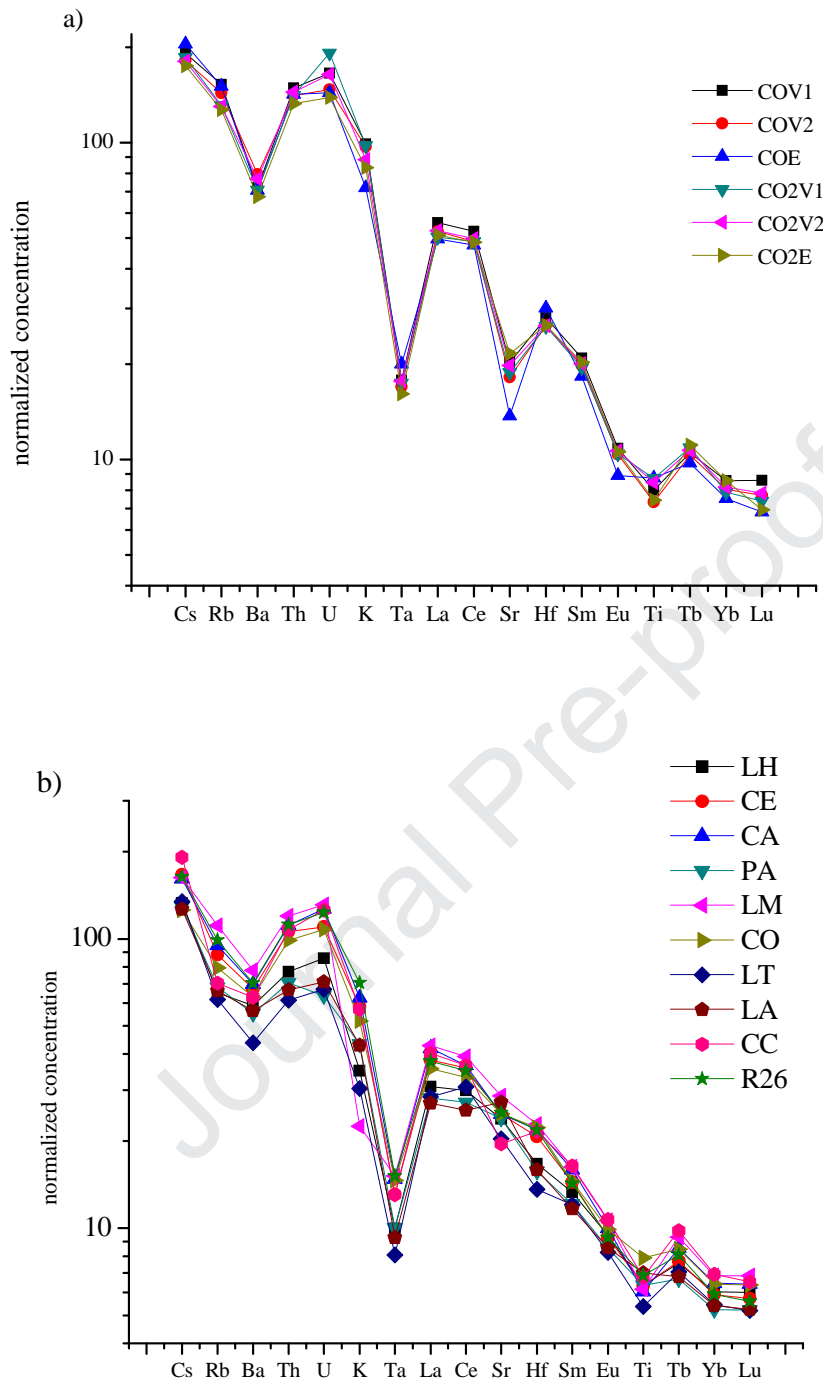


Figure 2: Normalised multi-elemental diagrams. a) Volcanic ash from Copahue volcano eruptions in 2000 (CO1) and 2012 (CO2), CO2V1 and CO2V2 are glass shards; CO2E: scoria, data were taken from Daga et al. (2017); b) soil samples from Copahue volcano area.

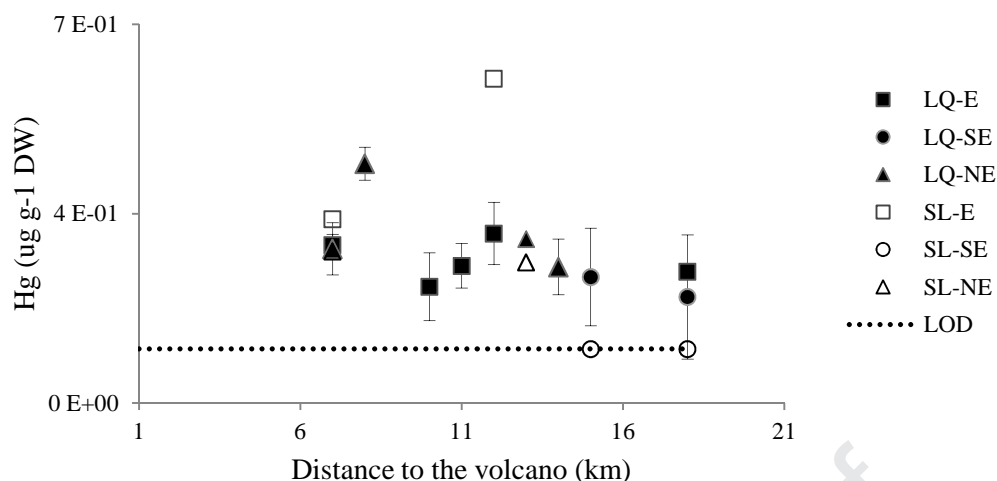


Figure 3: Total mercury concentrates in DW (average and standard deviation) vs volcano distance displayed according to ash plumes direction: northeast (NE), east (E) and southeast (SE), in soils (SL) and lichens (LQ), and limit of detection (LOD).

### 3.2. Lichens

Table 2 shows the elemental concentration (average and standard deviation values) of fruticose lichen thalli from CCv region. In Table S4 of Supplementary Materials the concentration and uncertainty values for the samples analysed from each sampling site are shown. *Usnea* and *Protousnea* genera did not show significant differences regarding semivolatile elements content. Relationship of the composition pattern of the thalli with the distance to the volcano was made using relevant Pearson's correlations (see Figures 4 and 5). Semivolatile elements were normalised by Mg (Figure 4) for the estimation of the relative abundance of volatile species in magmatic gas emissions and/or fumarole (Allard et al., 2000; Kodamatani et al., 2018). Besides, the possible oxidation reaction during the span of the plume was checked by Hg and Br linear correlation (See Figure 5).

Table 2: Elemental concentration expressed in  $\mu\text{g g}^{-1}$  dry weight basis of lichen samples from Copahue-Caviahue region (average values for each sampling sites)

	Concentration average	Standard deviation (SD)	Coefficient of variation (CV: %)
Sb	0.084	0.097	212
As	0.921	0.236	30.8
Ba	11.3	3.27	38.6
Br	4.51	2.33	66.6
Ca ( $\times 10^{-4}$ )	0.685	0.423	93.7
Ce	6.93	2.89	57.5
Cs	0.216	0.185	125
Co	0.473	0.106	28.7
Cr	1.06	0.351	40.4
Dy	0.768	0.352	52.0
Eu	0.179	0.079	53.8
Hf	0.147	0.064	53.2
Fe ( $\times 10^{-4}$ )	0.111	0.038	40.9
La	3.23	1.39	56.9
Lu	0.047	0.023	61.6
Mg	855	139	19.8
Mn	28.3	6.78	27.8
Hg	0.264	0.062	29.9
K ( $\times 10^{-4}$ )	0.279	0.059	25.0
Rb	5.854	2.625	54.7
Sm	0.884	0.406	60.5
Sc	0.993	0.295	40.3
Se	0.908	0.332	45.5
Na	398	145	48.5
Sr	25.8	12.0	71.0
S ( $\times 10^{-4}$ )	0.358	0.028	10.7
Ta	0.014	0.007	58.9
Tb	0.128	0.061	61.0
Th	0.282	0.146	67.9
Ti	225	84.1	48.5
U	0.068	0.025	47.7
V	3.37	1.17	43.6
Yb	0.365	0.178	59.8
Zn	20.3	4.14	26.4

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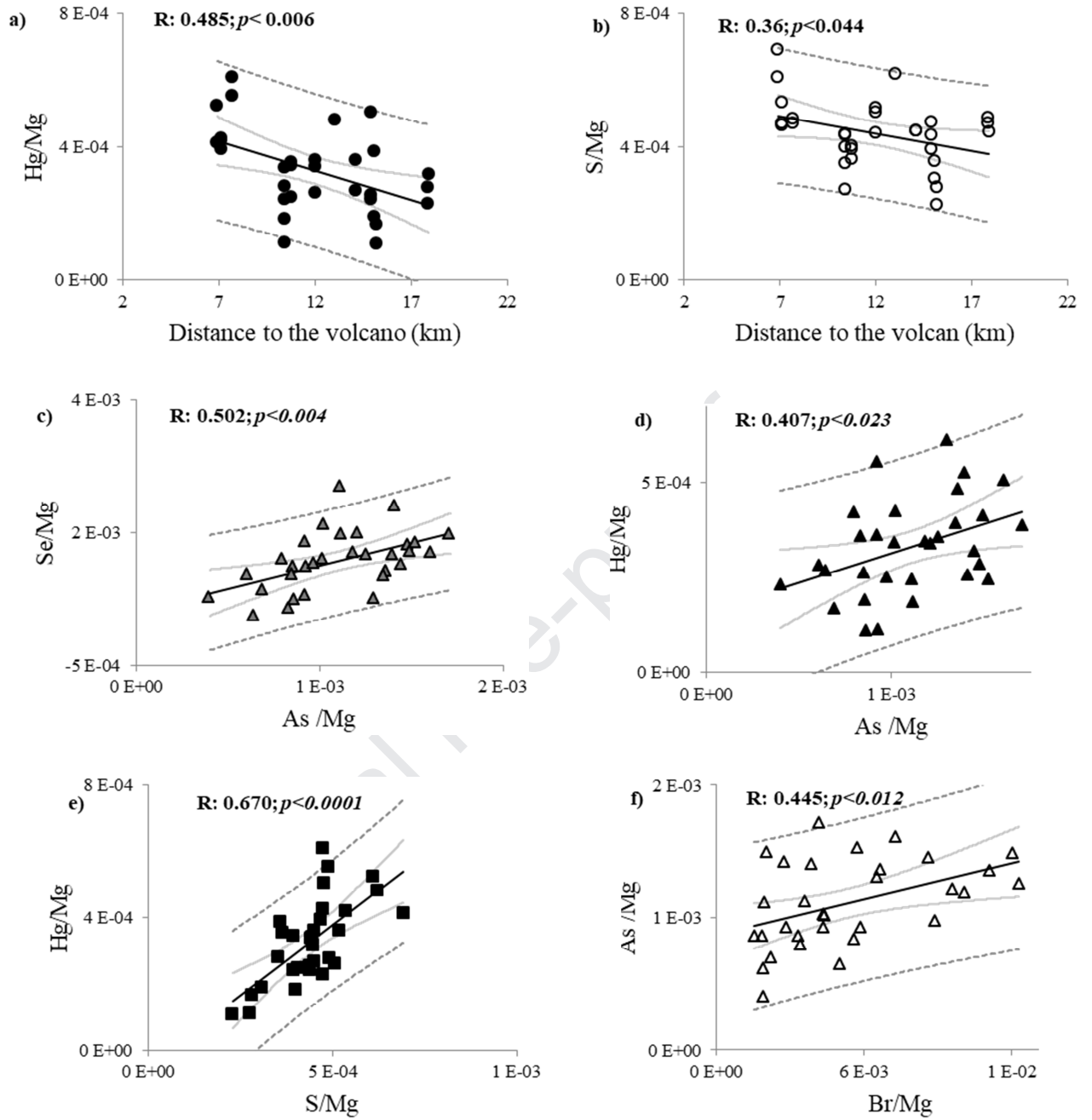


Figure 4: Concentrations were normalised by Mg, a) and b) show linear regression of As, Hg, Br, Se and S to volcano distance, and c) to f) show linear regression among normalised elements.

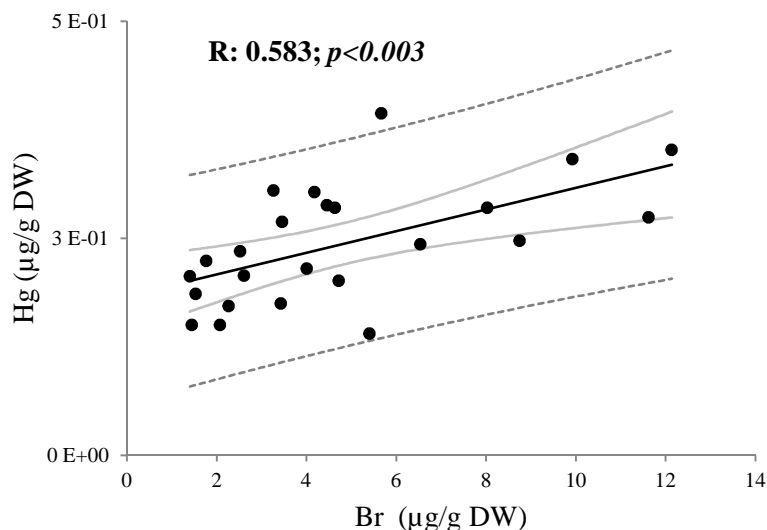


Figure 5: Linear regression of Br and Hg concentration in lichens.

#### 4. Discussion

The phenomenon of the propagation and dispersion of ash particles results from the interaction with the atmospheric movement and the stratification process. The ash column rises vertically and there is displacement on the horizontal axis, related to wind and turbulence. Variation of trace element concentration associated to particles with respect to crater distance cannot be modelled in a simplified manner by polynomial fits (Alvarez, 2012).

The volcanic semivolatile elements in soils did not correlate with the distance to the crater; the variations of total Hg concentration (THg) were in the range of the background values (Table 1). In three out of twelve sites of CCv, THg was above the limit of detection (LOD:  $0.1 \mu\text{g g}^{-1}$ ), at 6 km ( $0.26 \mu\text{g g}^{-1}$ ), 7 km ( $0.34 \mu\text{g g}^{-1}$ ) and 8 km ( $0.6 \mu\text{g g}^{-1}$ ) to the volcanic crater (see Figure 3). These values are within the range of the maximum acceptable concentration for agricultural soils ( $0.5$  to  $5 \mu\text{g g}^{-1}$ ; Pendas Kabata and Pendas, 2001). On the other hand, sulphur levels ranged from  $40$  to  $1720 \mu\text{g g}^{-1}$ , overlapping the range of international standards for agricultural soils ( $60$ - $600 \mu\text{g g}^{-1}$ ; Tabatabai, 1982) and Chilean volcanic soils ( $400$ - $1700 \mu\text{g g}^{-1}$ ; Aguilera et al., 2002).

Bromine has low natural background concentration and does not adsorb on negatively charged



soil minerals, but is easily transported by water. The toxicity to mammals, most freshwater organisms and most plants does not exist or is too low. In a strict sense, Br from natural sources is not an environmental pollutant. But Br levels have been associated with the explosive volcanic event in Puyehue-Cordón Caulle volcanic eruption (Bubach et al., 2012) and this could explain the high CV observed (Table 1).

Geographical distribution of Se is highly variable ( $0.01-7.0 \mu\text{g g}^{-1}$ ). For example, seleniferous soil regions with concentration of up to  $1200 \mu\text{g g}^{-1}$  were reported in United States, Canada, Colombia, United Kingdom, China and Russia (Chua Tan et al., 2016, and references therein). Selenium levels in CCv soils ( $0.45 \pm 0.08 \mu\text{g g}^{-1}$ ) were in the range of the reported world average. However, the highest Se content goes up ( $1.32 \pm 0.26$  and  $2.58 \pm 0.39 \mu\text{g g}^{-1}$ ) to 7 times the average. This corresponds to two samples at 12 km away from the crater; even so, these values are below the range for seleniferous soil.

The ash fall and soil resuspension by winds provide a constant exposure to volcanic materials for terrestrial ecosystems. The similar templates shown in Figure 2 of glass-fraction (2a) and soils (2b) confirm the origin of elements in the soil samples. In addition, the positive and negative correlations of semivolatile elements content in lichens (see Pearson correlations in Figure 4) together with the crater distance confirm that Copahue volcano is their source. The slope indicates the increment or decline of the element inventory into the plume.

The coefficient of variations of Hg in soil reached 43%, and was higher than in lichens (CV: 29.9%) with concentration ranging from  $0.14$  to  $0.46 \mu\text{g g}^{-1}$ . Marumoto et al. (2017) found major differences of THg concentration in volcanic ash samples depending on the eruptive type and/or different amount of ash fallen in the eruptive episodes. The temporal variation of THg contents were associated to other chemical components, such as  $\text{SO}_4^{2-}$  and  $\text{Ca}_2^+$ , in the ash ejected during the Strombolian eruptions; the volcanic activity was recorded using seismic signals (Marumoto et al., 2017). The Hg flux via ash falls has the same order as the annual atmospheric Hg deposition fluxes in Japan and represented large impacts of Hg accumulation on surface ecosystem. These results may explain the differences in THg content in soil and lichen samples according to distances relative to crater and direction of the preponderant plume in the

different CCv events, as shown in Figure 3.

The Hg uptake for lichens may respond to a first-order kinetic model, where the kinetic constant is related mainly to atmospheric conditions such as predominant flow direction and speed of the wind (Lopez Berdonces et al., 2017). In the Copahue area, the prevalent wind direction is from west to east. Nevertheless, during the events occurred since 2012 to 2016 most dispersions were from west to east and from west to southeast, while in previous events they were from west to northeast (Figure 1); consequently, it is possible to expect changes in the elemental composition of lichens affected by the different ash plumes.

Total Hg concentration in lichens was similar or higher than that in the soil, except for CC sites located at 10-11 km from the volcano, reflecting their ability to accumulate elements (Figure 3). The sampling sites located towards the northeast from the volcano were the only ones whose Hg concentration decreased with the crater distance (Figure 1). Typically, the particle size distribution in the volcanic plume is continuously evolving, whereas the pyroclastic fragments of great sizes are deposited around the volcano, and the smallest particles move upward by convection and fragmentation within the plume. The dispersed particles are carried downwind to very long distances from the volcano in the prevailing wind direction (Petrinovic et al., 2014). Likewise, the gasses released could be diffused throughout the way of the plume, as was observed by Paez et al., (2017) for the last Copahue eruptions cycle, and show a fingerprint to Hg release.

The flow patterns that govern the mechanisms which inject pollutant gasses into the air cause their accumulation like CO<sub>2</sub> at hazardous levels in topographic depressions 10-50 m deep (Chow et al., 2009). In addition, the volcanic plumes of low-altitude can sweep the ground through 10 km from the source; therefore, the reactive gaseous mercury (RGM) might deposit directly on soil and vegetation (Bagnato et al., 2014; Roland von Glasow, 2010). In our case, the highest Hg values correspond to LM and CO sites, both in the geothermal field at 7 and 10 km respectively from the crater (Figure 1a).

On the other hand, the Hg content of samples to the east and south-east from the volcano crater, about 15-18 km away, do not decrease significantly with the distance (Figure 3). All the

sampling sites east of the Copahue volcano are in the Río Agrio caldera (Figure 1b), a large basin surrounded by steep cliffs that surpass the 2000 m.a.s.l., while the two sampling sites located further south, LH and AR, are within the canyon called "Cajón del Huelcupén" (Figure 1 b). Besides the wind direction, the topography could have also been another factor that affected the Hg deposition patterns.

Sulphur, HCl, and HBr bearing gasses usually react and bring on extreme chemical loads dissolved in droplets of rain, absorbed or deposited on fine particles and snow

(<https://volcanoes.usgs.gov/vhp/gas.html>). The non-volatile elements in the ash clouds, such as Mg or other alkali metals (e.g.: Ca, Sr), become depleted in several orders of magnitude compared to volatile species (Br, Hg, Se). The ash particles cover a surface that can extend up to hundreds of kilometres, depending on the volume of material emitted, the intensity and length of the eruption, the direction and speed of the wind (Mather and Pyle, 2003).

The evolution of the crater-lake fluids during the twentieth century suggested a gradual awakening of the Copahue volcano. According to Varekamp et al. (2001), the Mg flux has been an excellent signal precursor to the eruption and a tracer for the rise (and dissolution) of new magma into the acid hydrothermal system. Linear regressions of the elements normalised by Mg are shown in Figure 4, as well as the distance to the volcano vs. Hg/Mg (Figure 4a) and S/Mg (Figure 4b). The plume containing gasses such as Hg and S is diluted expanding throughout air from the volcano crater. Measurements of Hg volcanic fluxes at the atmosphere were based on indirect or direct determination from SO<sub>2</sub> (or S) in the plume; for example, Bagnato et al. (2014, 2018) proposed Hg/SO<sub>2</sub> rate as an evolution signal of volcano activity. The behaviour of Hg and S gasses can also be represented by the ratio of concentration normalised by Mg, as shown in Figure 4c. This relationship, together with the fact that, according to laboratory experiments by Lodenius (2013), Hg is bioaccumulated in lichens evidences that these organisms can be good indicators of Hg from volcanic activity.

Chemistry studies in volcanic plumes were mostly related to sulphur oxidation reactions, not to halogen gasses. In the early plume, the Br<sub>2</sub> measurements showed rapidly formation of the BrO (bromine monoxide radical) and recently, BrCl (Bromine monochloride) formation was also

detected (Roland von Glasow et al., 2010; Roberts, 2017). These Br reactions were associated to Hg losses in several volcanic plumes and to reactive radicals through the atmospheric oxidation of GEM. Mercury from undifferentiated origin can be reduced and released again to the atmosphere, increasing the deposited oxidised mercury (Steffen et al., 2008). The relationship between Hg and Br in lichens from CCv was positive, as shown in Figure 5, and it supports the hypothesis of BrCl, BrO and GEM reactions and their successive deposition.

Arsenic and Se showed correlations among them and with Hg and S, but do not correlate with the volcano distance (Figures 4d, 4e). This indicated the diffusive nature of the process.

Furthermore, the four elements are linked to the formation of complex compounds and oxidation reactions, according to the results by Tamburello et al. (2015). These authors assert that Copahue volcano gasses are upheld underneath the crater-lake, where several oxidation compounds may be formed. The oxidation state is also an important control on the speciation and solubility of the species, such as with S and other trace constituents (Mather and Pyle, 2003).

In addition, chalcophile elements as As, Sb, and Se can be easily incorporated into molten S at the bottom of the volcanic lake (Mather and Pyle, 2003). The ascent of volcanic gasses passes through the S layer decreasing the temperature and solidifying the compounds into water. It has been reported that these elements were present in the dispersion gasses and ashes emitted in the Copahue events from 2011 to 2016 (Daga et al., 2017; Paez et al., 2017). Moreover, high SO<sub>2</sub>, H<sub>2</sub>S and halogen content were consistent with the leakage of hot magmatic fluids through the volcanic lake.

The S/Se/As ratios in the atmospheric particulate matter collected at about 60 km from Kilauea Volcano eruption site suggested that most eruptive As and S were transported as gasses.

Nevertheless, Se can rapidly be removed by condensation or absorption of particles like elemental Se and SeO<sub>2</sub> (Floor and Roman-Ross, 2012). The correlation showed in Figure 4c may be interpreted as the oxidised As and Se dissolved in rainwater and deposited on /incorporated by lichens.

Arsenic hydride (AsH<sub>3</sub>) is the most volatile of the inorganic species of As in fumarole gasses.

In several geothermal waters from Latin America, As and Cl remained in the liquid phase and showed a significant positive correlation (Lopez et al., 2012). Bromine was also present in the hot spring waters, for example, from Bandaiko, in the Kusatsu-Shirane volcano area, Japan (Kikawada et al., 2001), and it is possible that in the presence of elemental S there is arsenic bromination. This explains the correlation showed in Figure 4f.

In terrestrial ecosystems, airborne metals are mostly deposited in soluble or particulate forms which have a unidirectional flux towards vegetation and soil —e.g. their concentration in cryptogams are somewhat related to those in the bulk deposition (Bargagli, 2016). However, GEM can move continuously among air, soil and biota, and this bidirectional flux contributes to the lack of significant relationships between Hg concentrations in cryptogams (Aboal et al., 2010; Schröder et al., 1998). Concentration of GEM degassing from soil decrease exponentially as height above the ground increases, but the higher Hg accumulation in lichens growing on trunks may be explained by the Hg contribution from trunk flow waters leached from tree leaves and barks (Adamo et al., 2008). However, the Hg concentration in CCv lichens from the same sampling site but from different substrates (and height) did not show significant differences. GEM measurements performed in several Andean Patagonia regions suggested that the Hg impact comes from natural sources volcanic and forestall burning (average  $0.865 \pm 0.149 \text{ ng.m}^{-3}$ ) (Diéguez et al., 2017, 2019). The local GEM concentration pattern was characterised by higher GEM levels in spring and winter, when westerly winds were the most influential variable. High GEM was linked to air masses, which sweep Hg from the atmosphere going through numerous active volcanoes aligned in the Andes.

## 6. Conclusions

Sulphur, Se and Hg content in soil distribution were highly variable, and generally they overlap with ranges of international standards for agricultural and volcanic soils. The soil elemental content vs distance to the crater showed the highest values of Se at 12 km, and of THg from 6 to 8 km. The relationship of lichen Hg concentration with the volcano distance was checked for Hg/Mg and corresponds to the gaseous Hg chemical form. This fact, added to

the Hg correlation with volatile elements, such as Br and S, suggests that oxidation reactions could occur in the ash plume. This allowed the Hg deposition in vegetation and deposition/revolatilization in soil.

The results reflect that lichens were a good bioindicator of Hg fluxes from permanent Copahue volcanic emissions and eruptions. The studied area represents an excellent natural laboratory to investigate the impact of the entrance of Hg into the atmosphere.

#### **Conflict of interest**

The authors declare that they have no conflict of interest.

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