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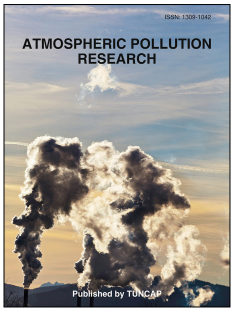

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Soledad Pérez Catán, Débora Bubach, María Inés Messuti, María Angélica Arribére, Sergio Ribeiro Guevara

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Credit Author Statement

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

Bubach, Débora F.: Formal analysis,Writing - Review & EditingInvestigation

Arribére MaríaAngélica: Formal analysis, Writing - Review & Editing, Project administration

Messuti, María Inés: Formal analysis, Writing - Review & Editing

Ribeiro Guevara Sergio: Funding acquisition, Project administration

Mercury and REE contents in fruticose lichens from volcanic areas of the South Volcanic Zone

Pérez Catán, Soledad[1]; Bubach, Débora[1]; Messuti, María Inés[2]; Arribére María Angélica[1, 3]Ribeiro Guevara Sergio[1]

[1]Laboratorio de Análisis por Activación Neutrónica, Centro Atómico Bariloche, CNEA, S.C de Bariloche, Argentina.

[2]INIBIOMA, UNComahue, CONICET, CRUB, Quintral 1250, 8400, S.C. de Bariloche, Argentina.

[3]Instituto Balseiro, Universidad Nacional de Cuyo, Bustillo 9500. 8400 S.C. de Bariloche, Argentina.

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Abstract:

Volcanic eruptions represent one of the natural sources of Hg along with evasion from the oceans. This work evaluates the influence of these sources on the Hg bioaccumulation by fruticose lichens. The sampling areas were located in nearby sites affected by recent volcanic activity in the Patagonia Andean range. Geological techniques such as the study of REE and multi-element patterns were used to identify the volcanic ash sources. The relationship among Hg and semi volatile elements with the distance to the emitting points were considered. In general, the results found in the lichens were in agreement with the provenance of glass fractions from volcanic eruptions in the influenced zone. The diagrams of lichen multi-elements concentration showed similar patterns for lichens taken from locations further south (near Hudson volcano) which were different from the lichens taken from the northern area (near Puyehue, Calbuco and Copahue volcanoes). The average values of LREE/MREE showed similar values in lichen samples taken from the north and south areas from Puyehue Cordon Caulle Volcanic Complex and the ranges of the volcanic glass particles expelled during the 2011 eruption. The results suggest that normalized patterns of the REEs in fruticose lichens might provide a proxy record of the elements released from a volcanic source. Correlations of concentration of semi volatile elements to the volcanic distances and to the Pacific Ocean showed that Hg and Sb bioaccumulation in lichens had one or both contributions.

1. Introduction:

Patagonian Andes is the region extending towards the tip of South America, on the border region between Chile and Argentina. It is part of a major volcanic belt known as Southern Volcanic Zone (SVZ), where volcanoes such as Calbuco, Chaitén, Copahue, Cordon Caulle and Hudson had eruptive events in the 20th century and at the beginning of the 21st century. Fruticose lichens species belonging to the Usnea genera have been used to evaluate semi volatile and lithophile elements released from volcanic events in Patagonian areas (Perez Catán et al. 2019 and Bubach et al. 2020, 2014, 2012).

Mercury (Hg) is a global pollutant which is a significant threat to ecosystems and human welfare worldwide due to the varied environmental fate of its different species like Hg0 (GEM), HgBr2, CH3-

Hg and C2H6-Hg (Driscoll et al. 2013). The emissions from active volcanoes are the only natural Hg sources of direct release into the atmosphere (Bagnato et al., 2007; Mather et al., 2003; Nriagu and Becker, 2003). The temporal variation of mercury emissions in gases or ash during volcano active stages has not been well recorded yet, and large uncertainties persist, especially on the active volcanoes in South America (Edwards et al., 2021; Nriagu and Becker, 2003; Slemr et al., 2015).

Gaseous elemental mercury is the predominant chemical form in the atmosphere (> 95 %), other chemical Hg forms (<5%) rapidly fall-out by wet and dry deposition, including reactive gaseous compounds and water soluble, for example: HgCl2, HgO, Hg(OH)2, HgBr2, CH3- and C2H6- (Lindberg et al., 1998, 2002). Atmospheric Hg monitoring based on direct instrumental measurements, has been carried out in several sites around the world (LopezBerdonces et al., 2017;Higueras et al., 2005). Nevertheless, this instrumental data is extremely variable given that surface volatilization rates depend on several factors such as light, temperature, soil moisture, vegetation cover, barometric pressure, cloud coverage and wind.

Lichenized fungi (lichens) are widely used as air quality bioindicators; they are suitable as tools in biogeochemical explorations since they are natural filters of atmospheric matter such as precipitation, fog and dew, dry deposition and gaseous absorption. They can, effectively, intercept airborne particles and aerosols from natural or anthropic sources (Bargagli and Mikhailova, 2002) and bioaccumulate elements depending on the thallus characteristics (Perez Catán et al. 2019; Bargagli, 2016;). According to Bargagli (2016), lichens thalli analysis is a valuable tool for Hg deposition studies in areas where volcanic activity has been manifested as geothermal fields and eruptions, pyroclastic and lava. Additionally, retrospective investigations have shown that lichens reflect atmospheric Hg loads and time-integrated Hg deposition rate (Zvěřina et al., 2018) and the Hg isotopic composition may be used to trace the sources contributions (Carignan et al., 2009) because they have ideal accumulative characteristics such as slow-growing rate and longevity.

The Rare Earth Elements (REEs) are considered immobile during most crust geological processes therefore they are used as tracers for a variety of processes in cosmochemistry, igneous petrology, and sedimentology (Chiarenzelli et al 2001). Generally, the lichens occurring in the same area show similar ratios of lithophile elements (Grasso et al. 1999) and the REE contents in lichen have been used to link with its source by linear regression (Ribeiro Guevara et al. 2004; Grasso et al.1999). Additionally, REE normalization procedures have been applied to distinguish effects from different geological basement or substrate in lichens (Agnan et al., 2014).

Volatile or semi-volatile elements such as Sb, As, Br and Se are present in the atmosphere from several sources, including marine spray, carried by the winds and incorporated by bioindicators such as lichens (Bargagli, 2016). The analysis of these elements, including Hg, and their relationship with the sea distance is a tool permits identifying this source as was observed by Perez Catán et al., 2020 in lichens from Clearwater Mesa, James Ross Island, Antarctica.

The goal of this study is to identify the relationship of mercury and its connection to volcanoes and atmospheric transportation from the Pacific Ocean. This is achieved by comparing elemental contents of the fruticose lichens from North Patagonia. The elemental concentrations in the bioindicators were analyzed applying REE normalization strategies to link the input to the provenance. Likewise, Hg, volatile and semi-volatile elements were studied through their relationship to lithophilic origin, volcanic and Pacific Ocean distances.

2. Materials and Methods

2.1. Sampling areas:

Entire thalli of fruticose lichens (2.5 to 3 cm) represented by *Usnea* and *Protousnea* species were collected in certain areas of the Argentina-Chile borderline according to the screening of particles dispersed by the predominant winds (varying with a general trend from Northwest to Southeast) and their availability at the sampling sites. A number of 10 to 15 lichens were collected by means of random walk encompassing 1 km^2 for each sampling site in March 2017. Additional data sets, ranging from 11 to 13 sites published by Bubach et al. (2020; 2014) were taken for this assessment corresponding to Puyehue Cordon-Caulle (PU) 2011 event, and the Copahue volcano (CO) from 2011 to 2017 (Table S-1 Supplementary Material). Figure 1 shows the study sites: Caviahue-Copahue(CO), Parque Nacional NahuelHuapi 33 to 115 km from the Puyehue Cordon-Caulle Volcanic Complex (PU) and in Bella Vista Mountain (BV) at an intermediate distance of 80-100 km, approximately, from PU and Calbuco Volcano; in the Epuyén-El Bolsónarea (EP) at 120 km away from Chaitén Volcano, and the area between the international crossings Los Huemules and Río Jeinemeni, Balmaceda (BA) and Mallín Colorado (MC), between 60 to 100 km from Hudson Volcano in Aysén Region, Chile.

2.2. Sample preparation and analysis:

Lichens were cleaned and analyzed, following the methodology by Bubach et al. (2012). The samples were cleaned to evaluate the bioaccumulated elements, based on the recommendations of the International Atomic Energy Agency (IAEA) working group (Smodiš and Bleise, 2002). First, dust and substrate were removed under microscope and then, the thalli were rinsed with ASTM grade 1 water with extremely short (1-2 seconds) immersion time to prevent chemical breakdown or ions solubilization in the water. Afterwards, samples were left to dry in a laminar flow hood or by freeze-drying, followed by grinding using liquid nitrogen. Aliquots of pooled 15 lichens thalli (n=3) for each site were put in sealed quartz ampoules to undergo Instrumental Neutron Activation Analysis (INAA) at the RA-6 nuclear reactor (MTR type, 1 MW thermal power). The elements determined were: antimony (Sb), arsenic (As), barium (Ba), bromine (Br), caesium (Cs), cobalt (Co), Hg, selenium (Se), thorium (Th), uranium (U), and zinc (Zn); the essentials calcium (Ca), iron (Fe), potassium (K), and sodium (Na); the trace elements hafnium (Hf), rubidium (Rb), scandium (Sc), strontium (Sr), and tantalum (Ta); and the light-REE (LREE) cerium (Ce), lanthanum (La), neodymium (Nd), middle-REE (MREE) europium (Eu), samarium (Sm), terbium (Tb), and heavy-REE(HREE) lutetium (Lu), and ytterbium (Yb). Analytical quality control (QC) was done using Lichen Reference Material (IAEA 336) showing good agreement with the recommended values (Table S-2 Supplementary Material).
Scanning electron microscopy (SEM-EDX) was performed in FEI Nova Nano SEM 230 and Philips 515 SEM with energy-dispersive X-ray analysis (EDAX) Genesis 2000, for complementary techniques to confirm the presence of ash particles and integration into the thalli on cleaned lichen samples.

2.3. Data analysis:

The "spider pattern" is a multi-elemental diagram in which the concentrations of elements are normalized by reference data such as the primitive mantle or chondrite (McDonough and Sun, 1995) and allows to identify the origin of the particulates. The diagrams are constructed with the normalized values represented on a logarithmic scale as a function on the increasing incompatibility order from right to left, typical for the mantle that has undergone partial fusion. Deviations from the general trend are known as anomalies and they characterize a specific process.

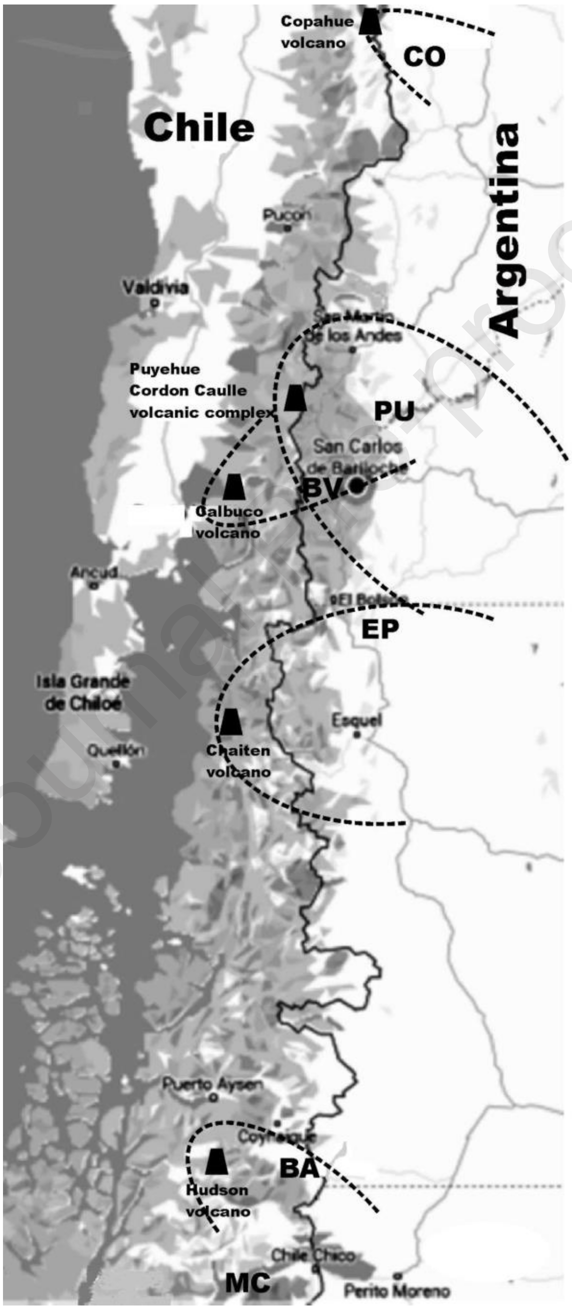

Fig. 1: Locations of the sampling areas from North to South: Copahue (CO); Puyehue-CordónCaulle volcanic complex (PU and BV: Bella Vista Mountain); Epuyén valley (EP) and, Los Huemules and Río Jeinemeni (BA and MC). The signals in dotted lines indicate the prevalent ash plume direction of

volcanic events in North Patagonia from 2011 to 2017; triangles indicate Puyehue-CordónCaulle volcanic complex and Copahue, Calbuco, Chaiten and Hudson volcanoes.

These diagrams as well as REE geochemical ratios were used to associate the elemental contents of lichens with volcanic events. The concentrations of elements in lichens were normalized according to Chiarenzelli et al. (2001) and Agnan et al. (2014) using the equation:

$$X_N = \frac{X_s}{X_{Ref}} \quad \text{Eq (1)}$$

Where X_N is normalized concentration of the element X, the subscripts indicate the X concentration in the lichen sample (*s*) and the chondrite as (*Ref*). The normalization by reference values is extensively used to identify sources of specific rocks or processes in geoscience studies e.g.: tephra layer, sedimentary deposits or solid cores (Daga et al. 2017; McDonough et al. 1995) and they are found in McDonough and Sun (1995). In order to connect the elemental concentrations in lichens with the volcanic emissions, the geochemical normalized composition of the glass fractions expelled by volcanoes of the areaswere taken from published data from Daga et al. (2017, 2014), D'Orazio et al. (2003) and Naranjo and Stern (1998), respectively. Several of these multi-element diagrams are shown as Supplementary Material Fig S-1, S-2 and S-3.

Spearman correlation analysis was performed to evaluate the concentration variations of the Hg, As, Br, Sb and Se on lichen, with distances of potential sources, volcanic or ocean, using XLSTAT program (copyright 1995-2009). Bilateral test with a significant coefficient is set at the 0.05 level.

3. Results:

Lichen thalli can capture particles that fall on the surface incorporating them in between cortex and medulla, as shown in Fig 2.

Figure 3 shows the multi-elemental composition of CO and PU lichens normalized with chondrite corresponding to sampling sites at different distances from the volcanic source. The Nd, Ti and Lu concentrations were not incorporated in this figure because their values were below the detection limit. In both cases, CO and PU had coefficients of variation that reached up to 50%, but each pool of samples was associated to a specific volcanic eventshowing a repetitive pattern of the multi-element diagrams that differed from the other volcano. Figure 4 shows the comparison of multi-element diagrams made with mean values of normalized concentrations of each studied area (CO, PU, EP, BE, BA and MC)". Normalized diagrams have a decreasing pattern that exhibit, as a rule, a deviation to the normal trend, called anomalies. The anomalies have been used to determine provenances of particlesamples or rocks in an impacted area with a volcanic event. The sample/chondrite values of elements Hf, Nd, K, Ta, Th and U presented on Table 1 justify the differentiation of PU, CO and MC samples from the others (Fig. 3 and Fig 4); minor differences were detected among BV, EP and BA by U, Lu and Yb., REE patterns (chondrite normalized) among studied areas in Fig. 4 show differences on the Eu and Sm which are considered as anomalies.

Table 1: Ratios of elemental concentrations of sample to chondrite in lichen samples corresponding to: Copahue-Caviahue (CO), Parque Nacional NahuelHuapi (PU and BV); Bolsón-Epuyen (EP) and Aysén (MC and BA).

Elements	Sites					
	CO	PU	BV	MA	BA	MC
Th	2.58	1.26	0.217	0.210	0.134	5.96
U	1.36	1.28	0.256	0.103	0.154	3.20
K	2.84	3.72	2.67	1.44	1.48	1.96
Ta	0.093	0.062	0.018	0.017	0.013	0.299
Hf	0.066	0.060	0.014	0.010	0.007	0.124
Ti	116					
Yb	0.126	0.075	0.009	0.010	0.006	0.131
Lu	0.114	0.067				

Reference values published for the Eu anomaly and ratios of La/Sm and La/Yb of the glass fractions corresponding to volcanic events from 2008 to 2017 of the North Patagonian, Argentina, are in agreement with the data of lichen samples on Table 2. The averages of LREE/MREE in lichens samples of CO, PU, BV and BA match the ranges for glass fractions from Puyehue Cordon Caulle Volcanic Complex (2.12-2.50) while both REE rates of the EP are similar to glass fraction of the

Chaitén Volcano. Considering the standard deviation of La/Sm ratios, the MC (2.70 ± 0.27) value agrees to PU (2.56±0.38).

The ranges of Eu anomalies of the lichens from CO (0.53-0.73). PU (0.53-1.31) and BV (0.4-0.5) areas are also in agreement with the tephra from the Puyehue event. Regarding EP. BA. and MC areas. Europium anomaly came near to products dispersed by the Chaitén volcano.

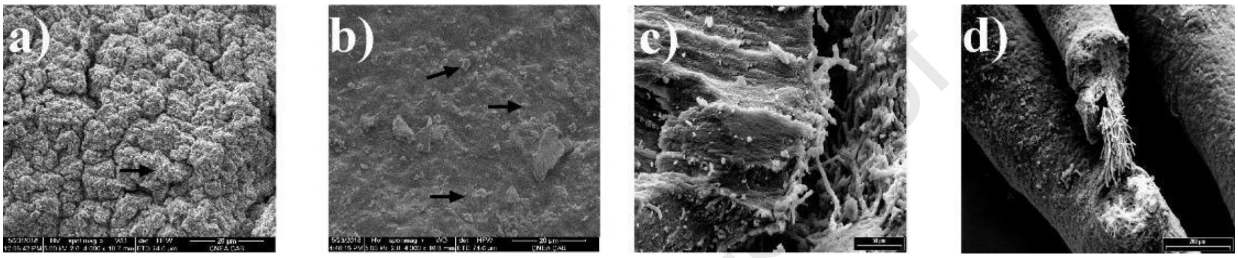

Fig. 2: Scanning Electron Microscope (SEM) photographs of glass shards belonging to volcanic plumes; a) and b) lichen surface. c) and d) into the thallus.

Spearman correlation tests among lichen concentrations of the semi volatile elements and La used as geochemical tracer (GT) were made with the distances to the potential sources. Table 3 shows the semi-volatile elements correlating among them, with TG and the volcanic distance (VOD). Pacific Ocean distances (POD) were only associated to Hg and Sb

Mercury concentrations among PU, BV, EP, BA and MC. showed a variation range from 0.081 ± 0.010 to 0.246 ± 0.020 $\mu g.g^{-1}$ DW. Taking into account the uncertainties, the variation does not show any trend (Fig. 5) while CO values were two times higher (0.140 ± 0.018 to 0.464 ± 0.041µg.g-1 DW).

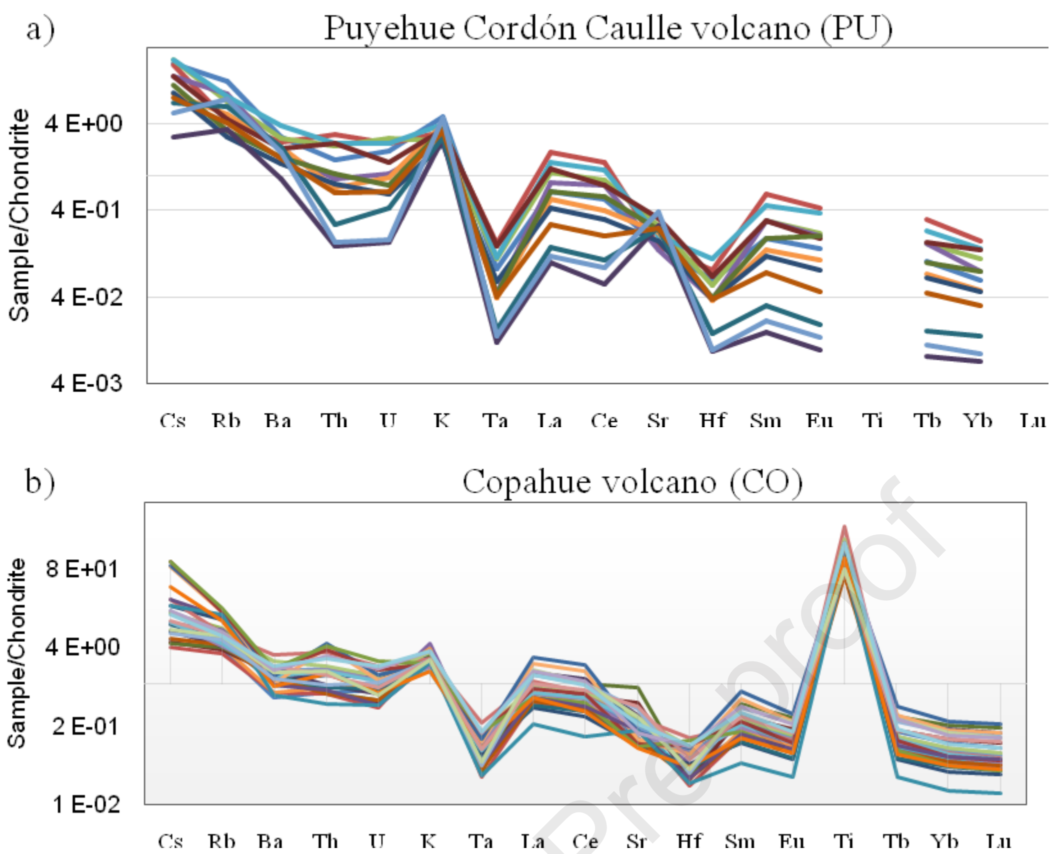

Fig. 3: Multi-element concentration diagrams of the lichen normalized to chondrite (McDonough and Sun. 1995) corresponding to 13 sites from 33 to 115 km from the sources (Bubach et al. 2020; 2014): a) PuyehueCordónCaulle volcano (PU) and b) Copahue volcano (CO).

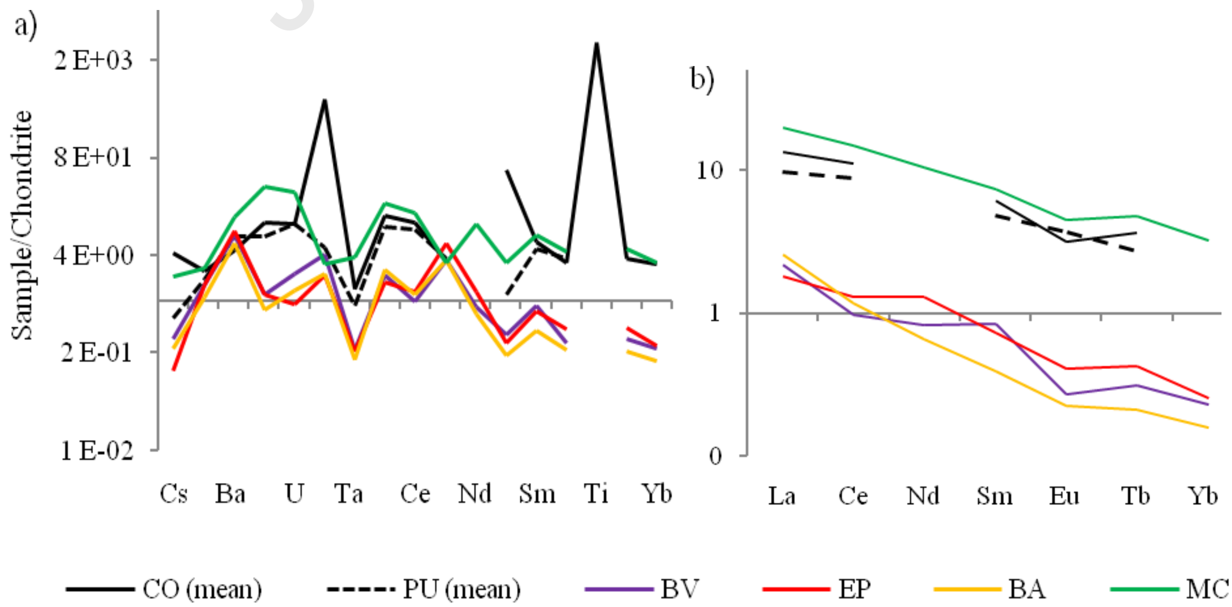

Fig. 4: Multi-elements (a) and Rare Earth Elements (b) diagrams of concentration in lichens corresponding to: Copahue-Caviahue (CO) from Bubach et al. 2020; Parque Nacional NahuelHuapi (PU from Bubach et al. 2014 and BV); Bolsón-Epuyen (EP) and Aysén (MC and BA). Normalization is to C1 chondrite values (McDonough and Sun. 1995; Wood et al.1979).

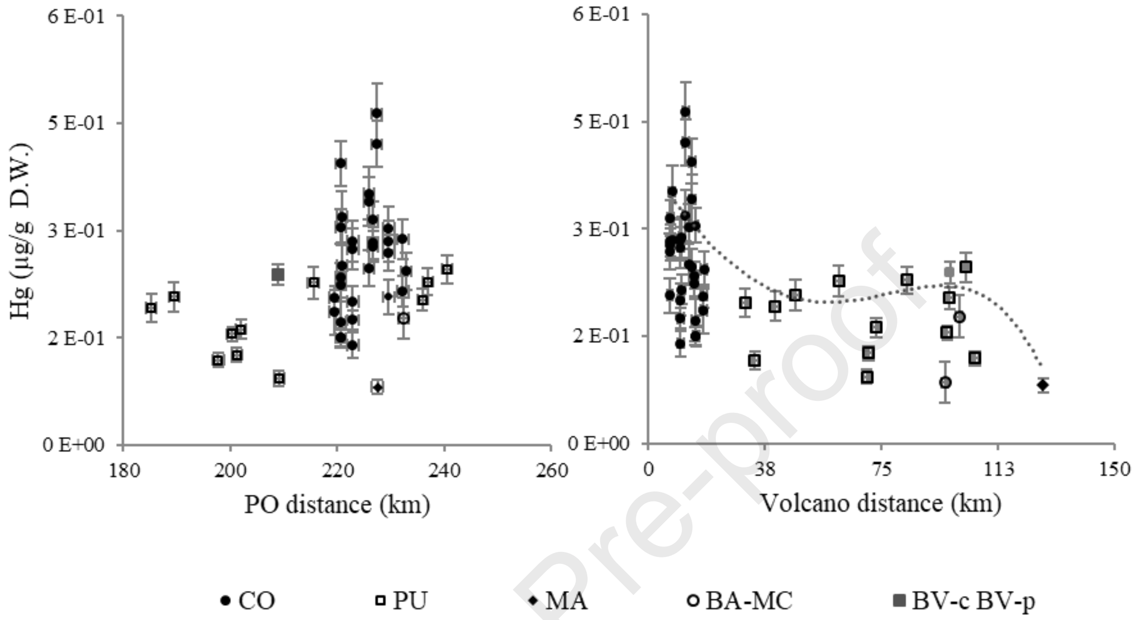

Fig. 5: Mercury concentrations in lichen samples (determined value and uncertainty) of sampling sites CO, PU, BV, EP, BA and MC against distances among sampling sites to (a) the Pacific Ocean and (b) to volcano crater that impacted the site in (Copahue, Cordon Caulle. Calbuco, Chaiten and Hudson).

Table 2: Ratios of LREE to MREE and HREE. Europium anomalycalculateby Eu/Eu*= Eu_N/ (Sm_N2*Tb_N)1/3. All the elemental concentrations were normalized to chondrite C1 (N) (McDonough and Sun. 1995).

	LREE/MREE	LREE/HREE		Eu/Eu*	References
	$[La/Sm]_N$	$[La/Lu]_N$	$[La/Yb]_N$		
Lichen samples					
CO	2.3±0.5		6.1±1.6	0.63±0.10	data Bubach et al. (2020)
PU	2.56±0.38	6.48±0.66	5.59±0.53	0.97±0.34	data taken from Bubach et al. (2012)

BV	2.60±0.26		9.5±1.0	0.45±0.05	this work
BA	2.49±0.25		7.11±0.71	0.67±0.07	this work
EP	6.53±0.65		16.4±1.6	0.70±0.10	this work
MC	2.70±0.27		6.22±0.62	0.70±0.10	this work
Dispersed volcanic glass fraction.					
Copahue Volcano (2012)	(4.0-4.3)*			(0.28-0.39)*	data taken from Daga et al. (2017)
Puyehue-CordónCaulle Volcanic Complex (2011)	(2.12-2.50)*	(3.74-4.18)*	(3.39-3.83)*	(0.55-0.60)*	Daga et al. (2014)
Hudson Volcano (1991)	4.90	9.00		0.41	data taken from Naranjo and Stern (1998)
Chaiten Volcano (2008)	(5.96-6.06)*	(17.6-18.8)*		(0.64-0.65)*	Daga et al. (2014)
Calbuco Volcano (1961)	1.24	2.42		0.87	Daga et al. (2014)
Calbuco Volcano (1961)	1.24	2.42		0.87	Daga et al. (2014)

* minimum-maximum range

Table 3: Spearman Correlation Matrix. The significant coefficient values of bilateral test (α=0.050). Lanthanum is used as geochemical tracer (TG)

	VOD	POD	Sb	As	Br	La (TG)	Hg	Se
VOD	1							
POD		1						
Sb		0.282	1					
As			0.632	1				
Br	-0.565		0.452	0.532	1			
La	-0.361		0.467	0.518		1		
Hg	-0.510	0.405			0.507	0.331	1	
Se	-0.687		0.302	0.562	0.521	0.509	0.458	1

4. Discussion:

The volcanic plumes are scattered following the preponderant - wind direction, the particle size distributed are continuously changing during the ash dispersion. The smallest pyroclastic particles fragmented within the plume fall at very long distances from the source. The dispersion process brought about a large impact on the environment mainly in the enclosed area indicated with dotted lines in Figure 1. These particles become embedded in the thalli much more easily in holes and are incorporated by the hyphae growth of fungal under moist or dry conditions. The effectiveness of trapping particulates varies by the growth form (Perez Catan et al. 2019; Rola et al 2016). Different lichen species could have different levels of bioaccumulation. The species of usnea could not be identified with certainty and the concentrations of elements varied significantly between area or source distances, not among sites of the same area. During sampling campaigns, usnea genus was the most abundant and present in all the sites. The fruticose growth form is efficient as bioindicator due to the area/volume ratio and scarce contact with the substrate (thalli extended up into a tufted or pendant branched structure) with respect to the other forms of growth which allows to evaluate airborne particles mainly (Bargagli. 2016). This emphasizes the importance of collecting only fruticose species from all sampling areas. Lichen samples examined by SEM-EDX showed particles on surfaces with different degrees of roughness and in the spaces between the cortex and medulla (see Fig. 2) even after the washing procedures. This emphasizes the importance of collecting only fruticose species from all sampling areas. Lichen samples examined by SEM-EDX showed particles on surfaces with different degrees of roughness and in the spaces between the cortex and medulla (see Fig. 2) even after the washing procedures. Lithophile elements usually show differential enrichment over light-REE middle-REE and heavy-REE. Under magmatic processes, a fractionated crystallization process occurs; part of the earth crust melts and subsequent differentiation by aggregation of elements occurs in several steps related to increasing the atomic number and the contraction of the atomic radius (Zepf V., 2013). This allows REEs to replace elements with similar ionic radius. e.g.: EuII by SrII, REEIII by CaII, ThIV. These tendencies are usually represented by ratios such as La/Sm and La/Yb and positive or negative anomalies as shown in Fig. 3 and 4, and Table 1 that connects the particles with their provenance. The REEs diagrams of lichens sampled in the Hudson volcanic area (BA and MC) follow the same pattern but differ from the rest as shown in Fig. 3.

Negative Eu anomaly is present in all patterns and represents varying degrees of plagioclase fractionation (Daga et al. 2017. 2014; Kratzmann et al. 2009; Naranjo and Stern 1998) and provides a link for the origin of the particles incorporated by the lichens. The Eu anomalies of glass fraction of the Chaiten volcano (Eu/Eu*= 0.64-0.65) and the Puyehue Cordon Caulle Volcanic Complex (Eu/Eu*= 0.55-0.60) were reported by Daga et al (2014). These events took place in 2008 and 2011 and the lichens were collected after these volcanic eruptions in September 2011 in PU and in other sampling sites where the gathering was done from March to April 2017. The Eu/Eu*anomaly of the Chaiten volcanic event is very similar to lichens of the EP, BA and MC areas, while the anomaly of the BV is in agreement with the Puyehue event. Moreover, averages of LREE/MREE in lichens samples of PU, BV, BA and MC match the ranges for the glass fractions from Puyehue Cordon Caulle Volcanic Complex (2.12-2.50) and the EP values of both REE rates are in agreement with the glass fraction of Chaiten Volcano. Whereas the REE rates and Eu anomaly of Hudson event 1991 do not match the MC and BA, both locations are close to the South and Southeast side to Hudson volcano. Unfortunately, the weak eruptive column during two months in 2011 ejected low amounts of pyroclastic particles mostly towards the East; the REE values of extra-fine thickness ash deposited were not measured (Amigo et al. 2012).

The Calbuco eruption in April 2015 was the third largest eruption occurred in Chilean Patagonia but several times smaller than the previous eruptions of Chaiten and Puyehue Cordon-Caulle. Nevertheless, the three events are in the list of volcanic eruptions of the 21st century presenting a Volcanic Explosivity Index (VEI) of 4 to 5; note that major eruptions have a VEI of 8 (Global Volcanism Program 2013). The eruptive events on the North Patagonian Andes for Chaiten and Puyehue events generated ash clouds over the Andes that, according to meteorological reports, transported volcanic aerosols through the world and reached, once again, the source area after 10 days. The dispersion models predicted contaminated regions and critical values at the south of 39°S in Argentina and Chile (Major et al. 2013; Collini et al. 2013). Conti et al. (2020) reported elemental concentrations of lichens from Tierra del Fuego, Argentina, monitored in 2011 and 2012 which was attributed to the Puyehue event.

The elemental concentration patterns in lichen samples normalized by chondrite reference values allowed the distinction of the volcano that influenced the elemental contents of the thalli samples (Fig. 3 and Table 1), and these patterns were independent of the distances between sampling sites and sources (Fig. 2). The correlations of semi-volatile elements with the TG shown in Table 2 confirm the volcanic origin, the REE diagrams and the evaluation of anomalies characterize the volcanic event.

Mercury concentrations in lichens for PU, BV, EP, BA and MC were in the range reported from different volcanic areas 0.01 µg.g-1 DW. to 0.200 µg.g-1 DW, Yellowstone National Park, USA. (Bennett and Wetmore. 1999) and Aisen Region XI. Chile (Monaci et al., 2012). The exceptions were the Hg concentration of the CO samples that increased up to two times more than these reported values. The samples taken in the areas of PU, BV could correspond to the Cordon Caulle event while the EP could be associated with the Chaitén eruption; the MC and BA samples correspond to Hudson by location. The mercury contents in the lichens of these sites did not show variations such as CO lichens (Fig. 5).

The correlations of the semi volatile elements with the distance could be considered as a fingerprint of origin provenance (Table 2). Hydrothermal vents located at the bottom of the ocean, also transfer chemicals from the earth's crust to the atmosphere. The mineralization in these hydrothermal vents is a kind of geysers of mineral-rich water at very high temperatures that emerge from fissures in the ocean floor. Bromine, As, Se, Sb and Hg are mainly in the volcanic gases and also from the oceanic cycle. The negative correlations agree with a volcanic Hg in which the concentrations decreased with the distances to the crater and increased when entering the Patagonian steppe (desert area) away from the coastline.

The volcanic inputs on the Hg contents in the CO lichens have been explained by the relation to the distance of the crater (Perez Catan et al. 2020). The higher Hg concentration range in CO lichens with respect to the rest may be associated with sampling sites proximity to both crater and geothermal emissions (<50 km). Nevertheless, the difference in the regime of precipitation among areas is a point to consider. The Patagonian Andes in the northern sector of the international PinoHachado pass are included in the Arid Andes. The CO sampling site is located in this region, where the Patagonian Mountain Range is found as a single block formed by two parallel mountain ranges in a north-south direction that receives humid air from the west and rain mainly from the Chilean side with snow in the high peaks. Orographic precipitation could be a consequence of the higher Hg values in CO. The other studied areas are located where the heights of the Andes decrease and are interrupted by valleys, passes and lakes, which allow the passage of rains in a narrow strip beyond which the winds blow from the west, producing the arid Patagonian zone.

On the other hand, the high GEM measurements made in the NHNP near the PU and BV sampling areas (Diéguez et al., 2017; 2019) were linked to the Pacific air masses that also sweep the Hg from the emissions of the active volcanoes in the Andes Mountains.

5. Conclusions:

An agreement was found among geochemical patterns of the multi-elements and REEs of the volcanic ashes and those corresponding to the compositions of the lichen thalli. This suggests that the normalized patterns of the elemental composition of fruticose lichens might provide a proxy record to identify the contamination from the volcanic sources.

According to dispersion graphs of Hg concentration vs distances, Copahue-Caviahue area was differentiated with respect to the others associated with volcanic influence in this area. In the lichens of NahuelHuapi National Park, Epuyen and Ayden regions, the effects of western winds from the Pacific Ocean in relation with Hg contents cannot be disdained. Further studies are necessary to confirm these trends.

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References:

Agnan, Y., Séjalon-Delmas, N., Probst, A., 2014. Origin and distribution of rare earth elements in various lichen and moss species over the last century in France. Sci. TotalEnviron. 487. 1-12.

Amigo, A., Silva, C., Orozco, G., Bertin, D., Lara, L.E., 2012. La crisis eruptiva del volcán Hudson durante octubre-noviembre 2011. XIII Congreso Geológico Chileno, Antofagasta, biblioteca.sernageomin.cl. pp. 457-459.

Bagnato, E., Aiuppa, F.P., Calabrese, S., D'Alessandro, W., Mather, T.A., Mc Gonigle, A.J.S., Pyle, D.M., Wangberge, I., 2007. Degassing of gaseous (elemental and reactive) and particulate mercury from Mount Etna volcano (Southern Italy). Atmos. Environ. 41, 7377-7388.

Bargagli, R., 2016. Moss and lichen biomonitoring of atmospheric mercury: A review. Sci. Total Environ. 572, 216-231.

Bargagli, R., Mikhailova, I., 2002. Accumulation of Inorganic Contaminants, in: Nimis, P.L., Scheidegger, C., Wolseley, P.A. (Eds.). Monitoring with Lichens - Monitoring Lichens. NATO Science Series, Series IV: Earth Environ. Sci. Vol. 7. Springer. Dordrecht. pp 65-84.

Bennett, J.P., Wetmore, C. M., 1999. Geothermal elements in lichens of Yellowstone National Park. USA. Environ. Exper. Bot. 42, 191-200.

Bubach, D.F., Dufou, L., Perez Catán, S., 2014. Evaluation of dispersal volcanic products of recent events in lichens in environmental gradient, NahuelHuapi National Park, Argentina. Environ. Monit. Assess. 186, 4997-5007.

Bubach, D.F., Perez Catán, S., Arribére, M.A., Ribeiro Guevara, S., 2012. Bioindication of volatile elements emission by the Puyehue - CordónCaulle (North Patagonia) volcanic event in 2011, Chemosphere 88, 584-590.

Bubach, D., Perez Catan, S., Messuti, M.I., Arribere, M.A., Ribeiro Guevara, S., 2020. Bioaccumulation of trace elements in lichens exposed to geothermal and volcanic activity from CopahueCaviahue volcanic complex, Patagonia, Argentina. Ann. Environ. Sci. Toxicol. 4, 005-015.

Carignan, J., Estrade, N., Sonke, J.E., Donard, O.F.X., 2009. Odd Isotope Deficits in Atmospheric Hg Measured in Lichens. Environ. Sci. Tech. 43, 5660-5664.

Chiarenzelli, J., Aspler, L., Dunn, C., Cousens, B., Ozarko, D., Powis, K., 2001. Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the Central Barrenlands, Nunavut, Canada. Appl. Geochem. 16, 245-270.

Collini, E., Osores, M.S., Folch Arnau, V.J.G., Villarosa, G., Salmuni, G., 2013. Volcanic ash forecast during the June 2011 CordónCaulle eruption. Nat. Hazards 66. 389-412.

Conti, M.E., Plà, R., Simone, C., Jasan, R., Finoia, M.G., 2020. Implementing the monitoring breakdown structure: native lichens as biomonitors of element deposition in the southern Patagonian Forest connected with the Puyehue volcano event in 2011-a 6-year survey (2006-2012). Environ. Sci. Pollut. Res. 27, 38819-38834.

D’Orazio, M., Innocentia, F., Manetti, P., Tamponi, M., Tonarini, S., González-Ferrán, O., Lahsen, A., Omarini, R., 2003. The Quaternary calc-alkaline volcanism of the Patagonian Andes close to the Chile triple junction: geochemistry and petrogenesis of volcanic rocks from the Cay and Maca volcanoes (~45°S. Chile). J. South Am. Earth Sci. 16, 219-242.

Daga, R., Caselli, A., Ribeiro Guevara, S., Agusto, M., 2017. Tefras emitidas durante la fase inicial hidromagmática (julio de 2012) del ciclo eruptivo 2012-actual (2016) del volcán Copahue (Andes del sur). Rev. Asoc. Geol. Argentina. 74, 191-206.

Daga, R., Guevara, S.R., Poire, D.G., Arribére, M., 2014. Characterization of tephras dispersed by the recent eruptions of volcanoes Calbuco (1961), Chaitén (2008) and CordónCaulle complex (1960 and 2011) in Northern Patagonia. J. South Am. Earth Sci. 49, 1-14.

Diéguez, M.C., García, P.E., Bencardino, M., D'Amore, F., Castagna, J., Ribeiro Guevara, S., Sprovieri, F., 2017. Four years of atmospheric mercury records in Northwestern Patagonia (Argentina): potential sources, concentration patterns and influence of environmental variables observed at the GMOS EMMA station. Atmos. Chem. Phys. Discuss. [preprint]. https://doi.org/10.5194/acp-2016-1076.

Diéguez, M.C., Bencardino, M., García, P.E. et al., 2019. A multi-year record of atmospheric mercury species at a background mountain station in Andean Patagonia (Argentina): Temporal trends and meteorological influence. Atmospheric Environ. 214, 116819.

Driscoll, C.T., Mason, R.P., Chan, H.M. et al., 2013. Mercury as a global pollutant: sources, pathways, and effects. Environ. Sci. Technol. 47, 4967-4983.

Edwards, B.A., Kushner, D.S., Outridge, P.M., Wang, F., 2021. Fifty years of volcanic mercury emission research: Knowledge gaps and future directions. Sci. Total Environ. 757, 143800

Global Volcanism Program 2013, Volcanoes of the World. v. 4.9.0 (04 Jun 2020). Venzke, E. (Ed.). Smithsonian Institution. https://doi.org/10.5479/si.GVP.VOTW4-2013, accessed in July 2020.

Grasso, M., Clocchiatti, R., Carrot, F., Deschamps, C., Vurro, F., 1999. Lichens as bioindicators in volcanic areas: Mt. Etna and Vulcano Island (Italy). Environ. Geol. 37, 207-217.

Higueras, P., Oyarzun, R., Lillo, J., Oyarzun, J., Maturana, H., 2005. Atmospheric mercury data for the Coquimbo region, Chile: influence of mineral deposits and metal recovery practices. Atmos. Environ 39, 7587-7596.

Kratzmann, D.J., Carey, S., Scasso, R., Naranjo, J.A., 2009. Compositional variations and magma mixing in the 1991 eruptions of Hudson volcano. Chile. Bull. Volcanol. 71, 419-439.

Lindberg, S.E., Hanson, P.J., Meyers, T.P., Kim, K.H., 1998. Air/surface exchange of mercury vapor over forests the need for a reassessment of continental biogenic emissions. Atmos. Environ. 32, 895-908.

Lindberg, S.E., Brooks, S., Lin, C.J., Scott, K.J., Landis, M.S., Stevens, R.K., et al., 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. Environ. Sci. Tech. 3, 1245-1256.

López Berdonces, M.A., Higueras, P.L., Fernández-Pascual, M., Borreguero, A.M., Carmona, M., 2017. The role of native lichens in the biomonitoring of gaseous mercury at contaminated sites.

J. Environ. Manager. 186, 207-213. https://doi.org/10.1016/j.jenvman.2016.04.047.

Major, J., Lara, L., 2013. Overview of Chaitén Volcano, Chile, and its 2008-2009 eruption. Andean Geol. 40, 196-215.

Mather, T.A., Pyle, D.M., Oppenheimer. C., 2003. Tropospheric Volcanic Aerosol in: Robock. A., Oppenheimer. C. (Eds.). Volcanism and The Earth's Atmosphere. Geophysical Monograph 139 (American Geophysical Union. Washington. DC). 189-212.

McDonough, W.F., Sun, S., 1995. The composition of the Earth. Chem. Geol. 120, 223-253.

Monaci, F., Fantozzi, F., Figueroa, R., Parrab, O., Bargaglia, R., 2012. Baseline element composition of foliose and fruticose lichens along the steep climatic gradient of SW Patagonia (Aisen Region, Chile). J. Environ. Monit. 14, 2309-2316.

Naranjo, J.A., Stern, C.R., 1998. Holocene explosive activity of Hudson Volcano, southern Andes. Bull. Volcanol. 59, 291-306.

Nriagu, J., Becker, Ch., 2003. Volcanic emissions of mercury to the atmosphere: global and regional inventories. Sci. Total Environ. 304, 3-12.

Perez Catán, S., Bubach, D., Messuti, M.I., 2019. A new measurement tool to consider for airborne pollutants evaluations using lichens. Environ. Sci. Pol. Res. 26, 1-4

Perez Catán, S., Bubach, D., Arribere, M., Ansaldo, M., Kitaura, M.J., Scur, M.C., Lirio, J.M., 2020. Trace elements baseline levels in *Usnea Antarctica* from Clearwater Mesa, James Ross Island, Antarctica. Environ. Monit. Assess. 192 (4): 246.

Ribeiro Guevara, S., Bubach, D., Arribere, M.A., 2004. Tracing mercury sources in NahuelHuapi National Park, Patagonia, Argentina, using lichens as atmospheric bioindicators. International Atomic Energy Agency, Vienna (Austria); 156 p; 2003; p. 76; International conference on isotopic and nuclear analytical techniques for health and environment; Vienna (Austria); 10-13 Jun 2003; IAEA-CN--103/010P; PROJECT IAEA ARG/7/006.

Rola, W.K., Osyczka, P., Kafel, A., 2016. Different Heavy Metal Accumulation Strategies of Epilithic Lichens Colonising Artificial Post-Smelting Wastes. Arch. Environ. Contam. Toxicol. 70, 418.

Slemr, F., Angot. H., Dommergue, A., Magand, O., Barret, M., Weigelt, A., et al., 2015. Comparison of mercury concentrations measured at several sites in the Southern Hemisphere. Atmos. Chem. Phys., 15, 3125-3133. https://doi.org/10.5194/acp-15-3125-2015

Smodiš, B., Bleise, A., 2007. IAEA quality control study on determining trace elements in biological matrices for air pollution research. J. Radioanal. Nucl. Chem. 271, 269-274.

Zepf, V., 2013. Rare Earth Elements. A New Approach to the Nexus of Supply. Demand and Use: Exemplified along the Use of Neodymium in Permanent Magnets. Springer Theses. Berlin. Heidelberg.

Zvěřina, O., Coufalík, P., Barták, M., Petrov, M., Komárek, J., 2018. The contents and distributions of cadmium and mercury and lead in *Usnea Antarctica* lichens fromSolorina Valley, James Ross Island (Antarctica). Environ. Monit. Assess. 190, 13.

HIGHLIGHTS

Volcanic pollutants identified by geochemical tracers determined in lichen samples.

Mercury and Sb content variation in lichens with Pacific Ocean distance.

Mercury deposition was related to western winds from the sea and volcanic emissions.

REE provide a proxy for recognizing natural pollution from events in Patagonian

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: