Mercury and REE contents in fruticose lichens from volcanic areas of the south volcanic zone

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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 (Pérez Catán et al., 2019; Bubach et al., 2012, 2014, 2020).

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 volcanic 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 (López Berdonces et al., 2017; Higuera 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 (Pérez Catán et al., 2019; Bargagli, 2016). According to Bargagli (2016), lichens thallus 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 (Zverina 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 crustal 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 Pérez 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 (2.5–3 cm) represented by Usnea and Protousnea species were collected in certain areas of the Argentina-Chile border line 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 10–15 lichens were collected by means of random walk encompassing 1 km² 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 volcanic complex (PU and BV) and Copahue volcano (CO) from 2011 to 2017; triangles indicate Puyehue–Cordon–Caulle volcanic complex and Copahue, Calbuco, Chaitén and Hudson volcanoes.

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 (Smolids and Bleise, 2007). First, dust and substrate were removed under microscope and then, the thalli were rinsed with ASTM grade 1 water with extremely short (1–2 s) 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 (Tables 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.

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:

$$X_{ni} = X_{n} \over X_{ref}$$

where $X_{ni}$ is normalized concentration of the element X, the subscripts indicate the X concentration in the lichen sample (n) 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 and Sun, 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 areas were 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.

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.

3. Results

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

Fig. 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 event showing a repetitive pattern of the multi-element diagrams that differed from the other volcano. Fig. 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 particle samples 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 (Figs. 3 and 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.

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.

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 μg 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 ± 0.041 μg·g⁻¹ DW).

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 Fig. 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 conditions.
several steps related to increasing the atomic number and the contraction 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. Lithophile elements usually show differential enrichment over 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-Caull. Nevertheless, the three events are in the list of volcanic eruptions of the 21st century presenting a Volcanic Explosivity Index (VEI) of 4–5; note that major eruptions have a VEI of 8 (Global Volcanism Program and Venzke, 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 and Lara, 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

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

<table>
<thead>
<tr>
<th></th>
<th>VOD</th>
<th>POD</th>
<th>Sb</th>
<th>As</th>
<th>Br</th>
<th>La (TG)</th>
<th>Hg</th>
<th>Se</th>
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<td></td>
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<tr>
<td>POD</td>
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<td>Sb</td>
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<td>As</td>
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<tr>
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<tr>
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<td>0.458</td>
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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).
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 Cordón 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 Catán 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 NHHNP 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


Credit author statement

Perez Catán, Soledad: conceptualization investigation, formal analysis, writing, original draft, ; Bubach, Débora F.: formal analysis, writing, review & editing, investigation; Arribére, María Angélica: formal analysis, writing, review & editing, project administration; Mesutti, María Inés: formal analysis, writing, review & editing; Ribeiro Guevara, Sergio: sampled analysis, funding acquisition.


