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Bioindication of volatile elements emission by the Puyehue–Cordón Caulle (North Patagonia) volcanic event in 2011

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ABSTRACT

The emission of volatile pollutants from the volcanic eruption of the Puyehue–Cordón Caulle complex (North Patagonia Andean Range) that started in June 4th, 2011, was investigated by bioindication means with the epyphytic fruticose lichen *Usnea* sp. The elemental composition of pooled samples made up with 10 lichen thalli were analysed by Instrumental Neutron Activation Analysis. Eleven sampling sites were selected within the impacted region at different distance from the volcanic source. Five sites were selected as they were already sampled in a previous study prior to the eruption. Two other new sampling sites were selected from outside the impacted zone to provide non-impacted baseline sites.

The elements associated with the lichen incorporation of particulate matter (PM) of geological origin were identified by linear correlation with a geochemical tracer (Sm concentrations). The elements associated with PM uptake were Ce, Eu, Fe, Hf, La, Lu, Na, Nd, Sb, Sc, Se, Ta, Tb, Th, U, and Yb. Arsenic and Cs concentrations showed contributions exceeding the PM fraction in sites near the volcanic centre, also higher than the baseline concentrations, which could be associated with permanent emissions from the geothermal system of the Puyehue–Cordón Caulle complex. The lichen concentrations of Ba, Ca, Co, Hg, K, Rb, Sr, and Zn were not associated with the PM, not showing higher concentrations in the sites nearby the volcanic source or respect to the baseline values either. Therefore, there is no indication of the emission of volatile forms of these elements in the lichen records. The lichen records only identified Br volatile emissions associated with the Puyehue–Cordón Caulle complex eruption in 2011.

1. Introduction

Volcanic eruptions are a well known source of elemental contamination to the atmosphere, in both regional and global scale. Volcanic ashes (tephras) and aerosols, either in volatile forms or condensed gases, contain pollutants such as antimony (Sb), arsenic (As), barium (Ba), bromine (Br), mercury (Hg), selenium (Se), thorium (Th), or zinc (Zn). Volcanic eruptions can be a mode of dispersal resulting in long-distance transport of pollutants through the atmosphere. Those will significantly impact not only regional sites near the volcano but also distant places, sometimes extending around the world (Nriagu, 1989; Hong et al., 1996; Delmelle, 2003; Vallelonga et al., 2003; Moune et al., 2006). The Northern Patagonia Andean Range is located in the Southern Volcanic Zone (SVZ), the product of the Nazca plate subduction under South American plate, an active volcanic arc from 33°S to 46°S. The Puyehue–Cordón Caulle volcanic complex is one of the active centres in the SVZ (Fig. 1), including various fissure vents with aligned domes and pyroclastic cones, and a geothermal system (Sepúlveda et al., 2004; Lara et al., 2006). Recently, a volcanic event started in the Puyehue–Cordón Caulle complex in June 4th, 2011, dispersing pyroclatic materials to the Patagonia steppe due to the West–East predominant winds (Fig. 1), with the last known eruption occurring in 1960 (Daga et al., 2010). The pyroclastic materials dispersed were already studied (Daga et al., submitted for publication) but there was no monitoring of volatile trace elements emission.

Lichens have been extensively used as bioindicators of atmospheric pollution world-wide (Garty, 2001), including monitoring of volcanic activity (Bargagli et al., 1989; Davies and Notcutt, 1996; Grasso et al., 1999; Varrica et al., 2000). Lichens can uptake non-biologically essential elements from the surrounding environment with no significant impact on their biological functions, storing them for long periods of time and acting hence as integrative natural samplers. The measurements of biologically essential elements, geochemical tracers, and potential pollutants in lichen samples collected from the region impacted by the volcanic activity will provide evidence on the emission of volatile elements during the volcanic event. The Nahuel Huapi National Park in southern Argentina is a protected region situated just across the international border from the Puyehue–Cordón Caulle volcanic complex in the direction of the predominant winds (Fig. 1), receiving the

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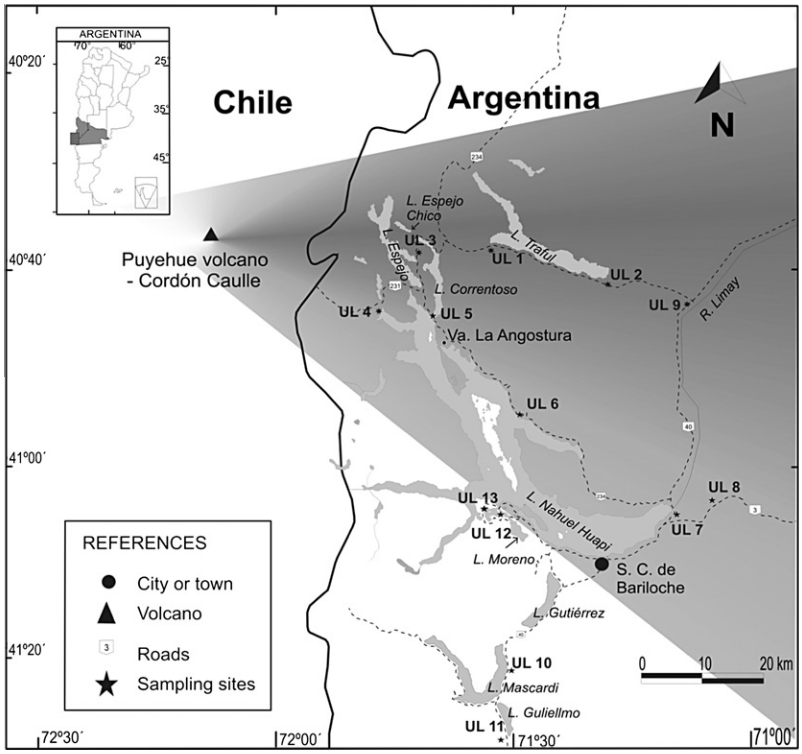

Fig. 1. The Puyehue–Cordón Caulle volcanic complex, North Patagonia Andean Range. The dark cone is the region impacted by the dispersion of pyroclastic materials in the volcanic eruption in June 4th, 2011, and thereafter, estimated from satellite photographs considering the variations of the plume position according to the wind direction.

direct impact of the volcanic products dispersed during the event. Previous research on the lacustrine systems belonging to the Park reported high metal levels, particularly Hg, and volcanic activity was a potential source (Ribeiro Guevara et al., 2010; Rizzo et al., 2011). Previous research included the study of lichens as bioindicators (Ribeiro Guevara et al., 1995, 2004). The recent Puyehue–Cordón Caulle eruption permits the comparison of post-eruption lichen samples with previous pre-eruption data. In this study, *Usnea* sp. were re-sampled from several original study sites (Ribeiro Guevara et al., 2004) as well as several impacted sites along a transect within the National Park and analysed for bioindicator markers of the recent Puyehue–Cordón Caulle eruption, to investigate the emission of volatile pollutants.

2. Materials and methods

The epyphytic fruticose lichen *Usnea* sp. was selected in this work due to its common distribution throughout the Nahuel Huapi National Park system. The taxonomic genus groups very similar species which are not easily distinguished in the field. Previous works on Nahuel Huapi studied different lichen species, namely the foliose *Candelariella vitellina*, *Hypotrachyna brevirhiza*, *Parmelia cunninghamii*, and *Physcia adscendens*, and the fruticose *Protousnea magellanica* and *Usnea fastigiata* (Ribeiro Guevara et al., 1995, 2004). The foliose lichen species had contents of particulate matter (PM) of geological origin reaching up to 40 wt.%, whereas the fruticose species had a much lower PM fraction. The PM trapped in the lichen structure interferes with the detection of volatile elements within the lichen tissues, so the fruticose species are better suited for volatile elements bioindication. Only *Usnea* sp. was found with similar biomass and development characteristics at most sites and were the most easily sampled with sufficient mass and consistency for analyses.

2.1. Sampling and sample preparation

The lichen collection was carried out two months after the eruption of the Puyehue–Cordón Caulle volcanic complex. The region with higher impact by the dispersion of the pyroclastic materials ejected by the volcanic source during this period was estimated from satellite photographs (Fig. 1), considering the spatial variation of the plume. Eleven sampling sites were selected within the impacted region along a transect from the volcanic source (Fig. 1). Five sites (UL4, UL5, UL6, UL8, and UL13) were selected as they were already sampled in a previous study prior to the eruption (Ribeiro Guevara et al., 2004). Two other new sampling sites (UL10 and UL11; Fig. 1) were selected from outside the impacted zone to provide non-impacted baseline sites.

Pooled samples were made up from 10 lichen thalli with similar development characteristics, collected from each site. The thalli were collected using clean techniques, e.g. plastic gloves, placed in clean polyethylene bags and stored at −20 °C temperature until processing for analysis. In the laboratory, the samples were allowed to warm up to room temperature and individual thalli were cleaned under microscope, using titanium and Teflon devices to remove external particles and extraneous organic matter. Afterwards, the samples were washed two times with nanopure water, then dried at room temperature in a laminar flow hood. After washing, the samples were cut and homogenised to fine powder, and finally freeze-dried until constant weight. Sample washing is not recommended by other researchers, considering that could modify the lichen composition. The elimination of the PM incorporated by the lichens, particularly the fine pyroclastic material, is a key aspect to evaluate the lichen uptake of volatile trace elements. The lichen washing was indispensable for a suitable PM cleaning in our case, although assuming a potential elimination of an elemental fraction. We consider here a previous research for a reference