



# Sustained effects of volcanic ash on biofilm stoichiometry, enzyme activity and community composition in North- Patagonia streams

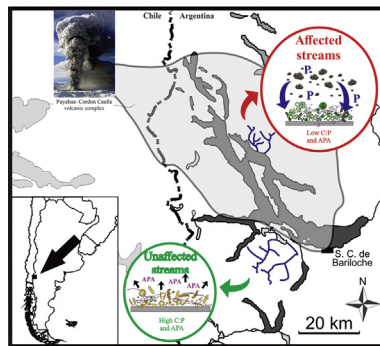
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## HIGHLIGHTS

- Volcanic deposits changed habitat and biofilm composition near the volcano.
- Affected streams had higher suspended solids and P concentrations than unaffected streams.
- Biofilm C:P ratio and alkaline phosphatase activity were lower in affected streams than in unaffected streams.
- Lower dissolved N:P ratio in affected streams led to higher Cyanobacteria biomass.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Volcanic eruptions are extreme perturbations that affect ecosystems. These events can also produce persistent effects in the environment for several years after the eruption, with increased concentrations of suspended particles and the introduction of elements in the water column. On 4th June 2011, the Puyehue-Cordón Caulle Volcanic Complex (40.59°S–72.11°W, 2200 m.a.s.l.) erupted explosively in southern Chile. The area affected by the volcano was devastated; a thick layer of volcanic ash (up to 30 cm) was deposited in areas 50 km east of the volcano towards Argentina. The aim of the present study was to evaluate the effect of volcanic ash deposits on stream ecosystems four years after the eruption, comparing biofilm stoichiometry, alkaline phosphatase activity, and primary producer's assemblage in streams which were severely affected by the volcano with unaffected streams. We confirmed in the laboratory that ash deposited in the catchment of affected streams still leach phosphorus (P) into the water four years after eruption. Results indicate that affected streams still receive volcanic particles and that these particles release P, thus stream water exhibits high P concentration. Biofilm P content was higher and the C:P ratio lower in affected streams compared to unaffected streams. As a consequence of less P in unaffected streams, the alkaline phosphatase activity was higher compared to affected streams. Cyanobacteria increased their abundances (99.9% of total algal biovolume) in the affected streams suggesting that the increase in P may positively affect this group. On the contrary, unaffected streams contained a diatom dominant biofilm. In this way, local heterogeneity was created between sub-catchments located within 30 km of each other. These types of events should be seen as opportunities to gather valuable ecological information about how severe disturbances, like volcanic eruptions, shape landscapes and lotic systems for several years after the event.

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## 1. Introduction

Explosive volcanic eruptions are extreme perturbations that affect ecosystems due to the ejection and emission of gases, ash, pumice, and lava (Franklin et al., 2000; Lindenmayer et al., 2010; Sousa, 1984). This material arrives in the biosphere directly from the Earth's interior, introducing new elements into ecosystems (Jones and Gislason, 2008; Óskarsson, 1980; Stewart et al., 2006; Witham et al., 2005). Many studies have examined how fresh ash deposition introduces a range of potentially toxic elements into the ecosystem, such as arsenic, copper, zinc, fluoride, and molybdenum (Cronin et al., 2014; Duggen et al., 2007; Ruggieri et al., 2011; Stewart et al., 2006). Ash and pumice can also deliver different key nutrient into the waters, such as iron or phosphorus, that can stimulate marine or lacustrine primary producers (Boyd et al., 2000; Frogner et al., 2001; Hamme et al., 2010; Modenutti et al., 2013). In addition to this enrichment effect, the increased concentrations of suspended particles (volcanic ash) in the water column may also positively affect phytoplankton growth by reducing photoinhibition in very clear lakes (Modenutti et al., 2013).

Besides the immediate effects, volcanic ash can also produce persistent effects in the environment lasting several years after the eruption (Dale et al., 2005). Volcanic material that falls into water bodies immediately affects the aquatic communities, while much of the material that falls inland can reach the streams decades after the event due to rain and snowmelt (Bisson, 2005). In this way, accumulation of ash in stream channels increases total suspended solids and changes the riparian zone, causing habitat loss that affects macroinvertebrate communities for years after eruption (Lallement et al., 2016; Miserendino et al., 2012). Additionally, following the initial physical effects, mechanical pyroclast disaggregation resulting from natural post-eruptive processes (i.e. avalanches, lahars, and fluvial transport) could produce new fresh particle surfaces with the increase of fine-grained particles that can also leach elements (Genereau et al., 2016). In this sense, there are very few studies investigating the effect of element inputs after the occurrence of volcanic eruptions on aquatic environments.

One of the elements responsible for fertilization effects after addition of ash is phosphorus (Modenutti et al., 2013). Phosphorus (P) recycling in streams is intimately associated with microorganisms attached to the bottom (the biofilm) (Dodds, 2003; Mulholland et al., 1994). In P-limited environments, algae and bacteria can acquire P from organic molecules by releasing extracellular enzymes, such as alkaline phosphatase, into the biofilm matrix (Sand-Jensen, 1983). Therefore, estimation of alkaline phosphatase activity (APA) can be used to detect P deficiency in aquatic ecosystems (Münster and Chróst, 1990). Since volcanic ash releases P, a decrease in P limitation would affect the N:P ratio (Modenutti et al., 2013) and this new environment would, in turn, affect biofilm composition since cyanobacteria would be favoured, increasing  $N_2$  fixation under an increased P supply (Marcarelli and Wurtsbaugh, 2006).

Northern Patagonia is an active volcanic region with historically high eruption frequency (Inbar et al., 1995). On 4th June 2011, the Puyehue-Cordón Caulle Volcanic Complex (40.59°S–72.11°W, 2200 m.a.s.l.) erupted explosively in southern Chile. The volcano produced 1.46 km<sup>3</sup> of rhyolitic volcanic material (or 0.2–0.4 km<sup>3</sup> dense rock equivalent pyroclastic deposits) (Silva Parejas et al., 2012), a similar amount to that erupted by Mount St. Helens in 1980. The total area (7.5 million hectares) affected by the volcano was covered by  $9.5 \times 10^{11}$  kg of pyroclast material, which fell differentially south-eastwards, depositing a thick layer (up to 30 cm) in areas 50 km east of the volcano towards Argentina (Gaitán et al., 2011). This event created an opportunity for the study of ecological disturbance following explosive eruptions. The aim of the present study was to evaluate the effect of volcanic ash deposits on stream ecosystems, analysing biofilm stoichiometry, APA and composition of primary producer communities four years after the eruption. Our hypothesis is that volcanic ash still releases P to the aquatic environment and this affects P content, APA and primary

producer's composition in the biofilm. We tested this hypothesis by comparing streams which received different ash discharges in the Nahuel Huapi catchment. Our predictions are: 1) streams with high levels of suspended solids (TSS) will have higher P concentrations both in the water and in the biofilm; 2) biofilms with low P availability in the environment will present higher levels of APA; and 3) differences in P availability will be reflected in the composition of primary producer communities.

## 2. Material and methods

### 2.1. Study area

After the eruption of the Puyehue, the predominant westerly winds of Patagonia generated a gradient (NW–SE) in the thickness of the deposited material (Elser et al., 2015; Gaitán et al., 2011) (Fig. 1). In the affected area (50 km from the volcano), the pyroclastic layers are mostly characterized by bimodal grain-size distributions, alternating lapilli layers capped by multiple fine ash layers (Pistolesi et al., 2015). The mineralogy and chemical composition of these deposits were studied immediately after the eruption and they are mainly composed of silicate glass (Caneiro et al., 2011; Castro et al., 2013; Shkinev et al., 2016). It is common that in fresh volcanic particles P occurs primarily in acid soluble forms and its solubility decreases with chemical weathering (Nanzoyo et al., 1993). Adsorption of volcanic salt aerosols is the main mechanism responsible for the presence of soluble compounds on volcanic particles (Smith et al., 1982; Smith and Kalff, 1983; Taylor and Stoiber, 1973).

Pristine (non-weathered) pumice produced by the Puyehue leached  $90 \mu\text{g P g}^{-1}$  (Modenutti et al., 2013). The most affected lakes showed an increase of total suspended solids and in light attenuation, higher P concentrations and phytoplankton biomass relative to pre-eruption conditions (Modenutti et al., 2013). By 2012, lake transparency had greatly recovered (Balseiro et al., 2014); however, thick pyroclastic deposits persist in the catchments (Fig. 2). Sampling was carried out in four streams according to the presence/absence of ash deposits (Fig. 1). We chose the streams based on the NW–SE gradient of deposit thickness and previous exploratory sampling, in order to select comparable systems regarding stream order, size, slope, vegetation cover and bottom morphology. Two types of streams were selected: Affected streams (A-streams), La Estacada (A1) and Ragintuco (A2), located closer to the volcano (approximately 50 km), with a 10-cm layer of ash in the floodplain; and Unaffected streams (U-streams), Goye (U1) and Casa de Piedra (U2), located 80 km from the volcano, without the presence of volcanic ash in the floodplain. The A-streams discharge into Lake Nahuel Huapi and have a N–S exposition. The U-streams discharge into Lake Moreno, which is connected with Lake Nahuel Huapi, and have a SW–NE exposition (Fig. 1). The streams are fourth order streams and drain pristine areas, where the only human activity is hiking.

Streambeds were dominated by a mixture of crystalline igneous, volcanic, and plutonic rocks with approximately 50% of boulders, 40% of cobbles, and 10% of gravel and sand, with volcanic deposits in the interstices of rocks in A-streams. The streams are surrounded by perennial native forests of *Nothofagus dombeyi* and *Austrocedrus chilensis*. The area receives approximately 2000 mm year<sup>-1</sup> as rainfall and snow, following a bimodal hydrological regime with high discharges in late autumn and spring (rainfall and snowmelt, respectively) and the lowest discharge in summer–early autumn.

### 2.2. Leachate experiment

In order to investigate volcanic deposits as a source of P in the environment, we performed a laboratory experiment in which we quantified P released from lapilli four years after the eruption. In addition, we assessed whether the effect of milling increased P leachate. We assessed the milling effect using two grain-size particles: Large size

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