

**“A mosaic of phytoplankton responses across Patagonia, the SE Pacific and SW Atlantic Ocean to ash deposition and trace metal release from the Calbuco 2015 volcanic eruption” by Vergara-Jara et al.**

The present study by Vergara-Jara and co-workers is based on collected ash from the 2015 Calbuco volcano emission and water samples from Reloncaví fjord from Patagonia (Chile) and seawater samples from south Atlantic. In this study, the authors did some leaching experiments using the collected ash and water samples (or deionized water) to understand the significance of fresh and aged ash in its efficiency in leaching trace elements (Fe, Cd, Pb, Ni, Cu, Co, Mn). Besides, to understand the leachability of bioavailable Fe, the Fe(II) fraction, the authors also performed some specific leaching procedures. Also, some additional leaching experiments were performed to understand the changes in major ion abundances and total alkalinity of water samples upon ash addition. Further, in order to understand the changes in primary productivity in the nearby oceanic basin (Atlantic Ocean), satellite data was used.

The present manuscript opens up a study on one of the important aspects in trace metal biogeochemistry: the role/impact of sporadic and random volcanic eruptions and ensuing ash fallout on leaching of trace elements in the surface ocean (and marginal) waters and associated effects on marine biological productivity. The authors have used lab-based leaching experiments to estimate the fraction of dissolved Fe (dFe) and Fe(II) that is susceptible to leaching from the ash. One of the most interesting results of this study is the reduction in release of Fe(II) with aged ash.

The manuscript is overall well written. The statements and arguments are mostly laid out clearly and easy to follow. However, I have some concerns with the present version of the manuscript. My concerns with the present version of the manuscript are two-pronged. These have been detailed as follows:

- 1) As is in the present version of the manuscript, section 2 (Materials and methods) is difficult to follow. When I started reading this section, I was looking for a common subsection detailing all the samples (and their sampling location) for the present study. Opening section 2, subsection 2.1 is placed well and describes the study area providing the regional details. However, I would like to suggest the authors insert a subsection 2.2, providing details of all the samples collected and analysed in the present work. In addition, there are some minor concerns with this section (section 2). For e.g. (i) this study is based on the changes in biogeochemistry of Reloncaví fjord and the Atlantic Ocean immediately after the eruption of Calbuco volcano. However, some samples from another location (Aysén fjord) were also discussed in the manuscript (line No. 184). This location has only been mentioned here and nowhere else in the manuscript. (ii) As mentioned in line 134, there is a mooring station located in Reloncaví fjord, its location is not known until late in the manuscript (Line 311).
- 2) I have some concerns regarding the leaching experiments done by the authors. As is the case in the present work, different leaching experiments were performed for different set of parameters (major ions, trace metals and Fe(II)). Why did the authors use different leaching procedures for different parameters in the present work? It was the same ash falling over the waters of the fjord and Pacific ocean. So, to see the combined effect of the ash falling on fjord waters, authors should have used similar leaching protocols for major ions, trace metals and Fe(II). Also, the authors have used deionized water for their leaching experiments for major ions. Why did the authors not consider using the *trace metal free seawater* for their leaching experiments? Also,

some of the methods are not clear. For the leaching experiments for major ions, the authors have mentioned correcting the abundances for initial water concentrations. Was this also done for trace metal leaching experiments? The authors have mentioned that for leaching experiments for major ions, they used both fjord waters and deionized water, but table 1 only provides results for leaching with deionized water. Also, I would highly appreciate if the authors can provide the basis for some of the parameters for the leaching experiments: for e.g., for the major ion leaching experiments, authors have taken 0.18 g ash with two size fractions (< 63 µm and 250-1000 µm). What is the basis for using these leaching experiment parameters? Also, I noticed some discrepancies in connection to the leaching experiments: earlier in the manuscript in the methods section, the authors described the leaching experiments for trace metals (dFe) and Fe(II) to be very similar, however, later in the manuscript, the authors described both the leaching experiments as not comparable.

Detailed comments following the ms structure:

Line 81: Insert “deposition” between “ash” and “on”.

Lines 86 to 90” Rephrase the sentence as “In contrast, there are several adverse effects of ash deposition on marine organisms that include: (i) metal toxicity (Ermolin et al., 2018), especially under high ash loading, and/or (ii) ingestion of ash particles by filter feeders, phagotrophic organisms or fish (Newcomb and Flagg, 1983; Wolinski et al., 2013)”.

Lines 92 to 94: Rephrase as: suggesting that “significant ash deposition on aquatic environments can also impact and perturb their carbonate system.”

Line 96: Insert “the” between “to” and “source”.

Line 96: Insert “abundance of” between “where” and “macronutrients”.

Lines 99 to 100: Rephrase as “In contrast to the 2013 Eyjafjallajökull plume over the North Atlantic, the 2015 ash plume over the region from the Calbuco eruption.....”.

Line 104: Replace “of” by “from”.

Line 121: Looking at the mean monthly river water flows, the Puelo river looks to be bigger/major than the Petrohué River.

Line 127: Replace “marine primary production high” with “ high marine primary production”.

Figure 1: Please label the scale in C.

Figure 1: Can you provide the areal extent of ash deposition from the eruption of Calbuco volcano in the figure.

Figure 1: Please show the location of Cochamó on the map.

Line 148: Can you kindly elaborate on what is meant by the surface of a plastic container?

Line 151: Please provide the location from where the south Atlantic seawater sample was collected.

Line 157: What was the duration for Mucosal stage?

Lines 167 to 168: Replace “shaken by hand” with “manually shaken”.

Line 167: Replace “into” with “to”.

Lines 174 to 175: How was the instrument calibrated. Could you please provide some more details?

Line 175: Replace “dissolution” with “leaching”.

Line 179: Replace “dessert” with “desert”.

Line 183: Insert “major” before “ions”.

Line 184: This is the only place in the manuscript where any sample from the Aysén Fjord is mentioned.

Lines 191 to 193: Rephrase as: “Samples were immediately analysed for total alkalinity ( $A_T$ ) via a potentiometric titration.....”.

Line 200: Please expand APHA.

Lines 203 to 206: At what station/location were these measurements made?

Line 204: How was the dissolved oxygen sensor calibrated?

Line 230: Replace “onto” with “of sampled water through”.

Line 232: Replace “was” with “were”.

Line 247: Could you provide a reference for significant spread of 2015 Calbuco ash to Pacific and Atlantic regions.

Line 269: Please provide the location of mooring station here. It has been mentioned later in line 311.

Figure 4: The May 16 diatom abundance is very high in two extreme stations in fjord: stations A and C, while it is lowest in station B (intermediately placed in the fjord). Can authors explain this?

Lines 303 to 305: As the data plotted on figure 4 shows, the lower diatom abundances were observed in middle station B (open circle) around May 15.

Figure 5: If discussing the brackish water leach experiments at first, place the results for brackish water on the left-hand side panel.

Table 1: It was earlier mentioned by the authors that for leaching experiments for major ions, both brackish water and deionized water were used. Table 1 only presents data for deionized water. Where are the results for leaching experiments with fjord brackish waters?

Figure 6: One of the data points (on all plots) at high ash addition (between 5 and 6 mg) has error in x-data (ash, mg). I assume the ash loading/addition was based on precise weight of ash added to test waters, so it must be known well.

Figure 6: Here, the authors have mentioned that effect of trace metal leaching upon ash addition was estimated by deducting the initial seawater trace metal seawater concentrations. This has not been mentioned in methods sections. Please provide these details in methods section.

Lines 393 to 395: This is an important point, should have been brought out earlier.

Lines 496 to 497: This is the first time the authors have discussed the relative impact of ash fallout on their stations in Reloncaví fjord. Can the authors discuss this earlier in the manuscript (in section 2)?

Lines 575 to 577: The south western Atlantic chl-a data also shows some significant excursions close to the Calbuco eruption. Also, once the chl-a dips to lowest values close to the Calbuco eruption, it again increases around April 25, concomitant with an increase in aerosol index. Is this due to atmospheric transport of Calbuco ash and its deposition over the region?