

Interactive comment on “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 Maximiliano J. Vergara-Jara et al.

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Q. Questions/comments R. Responses

With respect to the major concerns: changes have been made to the section 2 (Materials and methods), including a table with information from all the leaches conducted.

Q. As is in the present version of the manuscript, section 2 (Materials and methods)

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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). R. For Aysen fjord, we have highlighted in section 2.3, we changed the first paragraph to clarify why we were using that water and not Reloncaví fjord water (new lines 205-207). In simple terms, during our first visits to the main fieldsite (Reloncaví) the ash loading in water was extremely high, and we were concerned that even in the weeks after the main ash load diminished there may have been a legacy of ash in the water composition. It therefore made little sense to use Reloncaví water for ash leaches, so we collected water from a nearby system where any ash deposition was negligible.

Q. 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

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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. R. Different procedures are necessary for two reasons. First, with respect to Fe(II), Fe(II) has a short half-life at room temperature (> 1 minute in seawater). It takes at least one minute to measure the concentration using the most rapid available method (flow injection analysis with a continuous flow of sample). Thus any standard leaching protocol at room temperature will invariably measure very low levels of Fe(II) irrespective of whether any was released from ash, or not. Consequently, for Fe(II) analysis we ran experiments at low temperature. For remaining trace metals we opted for a room temperature leach to follow prior work. The leaches are therefore roughly comparable as both test the effect of ash addition on dFe release in seawater, but in the standard protocol the initial 'pulse' of Fe(II) detected in the chilled experiments has likely already decayed to some extent which cannot be quantified.

The condition of coastal seawater and offshore seawater are always (broadly speaking) very different with respect to trace element concentrations; much higher concentrations are present in coastal waters. The amount of metal that can be leached from ash into solution is very sensitive to the ambient concentration of Fe already present. For comparability with prior work, and to focus on the potential effect of ash on offshore trace metal dynamics (which is where any metal-fertilization would be expected to be most

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evident) we therefore used offshore seawater. The difference between TA and DIC anywhere in the ocean is far less pronounced than the difference in metal levels. Note that the DI experiment provides additional opportunity for comparison with similar studies (e.g. Jones and Gislason 2008), in addition to being more sensitive to the estimation of net leaching of major ions and macronutrients. Similarly, for trace elements, saline leaches are the most appropriate for our research question as Fe is not generally considered an important control on freshwater productivity, nor would it likely increase the net loading to coastal ecosystems from riverine inputs.

For the analyses of the data from experiments explained in section 2.3, the correction of the abundances for the initial water concentrations was done in order to focus on the ion inputs from the ashes and not in the total ion content from all the leachates. Because we were working with fresh water, we have to subtract the initial ion concentration after the experiment was done. Similarly for trace metal leaches, the initial concentrations in seawater are noted and deducted where concentrations are plotted as the change in concentration before/after ash.

The different ash size fraction used in section 2.3 were made in order to quantify accordingly the impact from different particles from the same sample, following the recommendations of Witham et al., 2005. The main constraint was the amount of ash available. Note that although the total mass of unhydrated ash was limited, the ash/water ratio for DI leaching experiments was of the same order of magnitude as for Jones and Gislason 2008. Note also that the single 45-125 μm size fraction used in J&G's experiment, although standardized across sites, was most likely selected based on the need to maintain circulation through a continuous flow reactor. The two size fractions used here represent standard mesh sizes, and were chosen for the principal purpose of demonstrating the proportionately greater effect of the fine fraction selecting the finest and coarsest fraction which we would still have enough material to work with. Finally, we note that grain size distribution will vary widely across any given ash plume, being the overriding factor in terms of comparing effects across eruptions.

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Q. Line 81: Insert “deposition” between “ash” and “on”. R. Line 81: recommendation accepted.

Q. 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)”. R. Lines 86 to 90: Now the new paragraph is as follow: “In contrast, apart from inducing light limitation, there are several adverse effects of ash deposition on marine organisms that go from metal toxicity 1- particularly under high dust loading 2- or more generally from the ingestion of ash particles by filter feeders, phagotrophic organisms or fish 3,4”.

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

Q. Line 96: Insert “the” between “to” and “source”. R. Line 96: suggestion accepted.

Q. Line 96: Insert “abundance of” between “where” and “macronutrients”. R. Line 96: suggestion accepted.

Q. 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. . . .”. R. Lines 99 to 100: suggestion accepted.

Q. Line 104: Replace “of” by “from”. R. Line 104: suggestion accepted.

Q. Line 121: Looking at the mean monthly river water flows, the Puelo river looks to be bigger/major than the Petrohué River. R. Line 121: It is. Now the rivers are mentioned in order of their flow.

Q. Line 127: Replace “marine primary production high” with “high marine primary production”. R. Line 127: suggestion accepted.

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Q. Figure 1: Please label the scale in C. Can you provide the areal extent of ash deposition from the eruption of Calbuco volcano in the figure. Finally, please show the location of Cochamó on the map. R. Figure 1: Figure 1 now has the scale labeled and the location of Cochamó town is marked on the map. Also, a new reference extent of the ash cloud is showed in Fig. 1 C (although note that the ash cloud changed from day-to-day). Now this new information is clarify in the text in section 2.1 at the end, the following paragraph was added: “The Chilean Geological-mining Survey (Servicio Nacional de Geología y Minería, SERNAGEOMIN) elaborated daily technical reports with information about the area of dispersion for the emitted ash (<http://sitiohistorico.sernageomin.cl/volcan.php?pagina=4&ild=3>). We used this information to create a reference aerial extent of ash deposition for the days after the eruption (Fig. 1, C).”

Q. Line 148: Can you kindly elaborate on what is meant by the surface of a plastic container? R. Line 148: A plastic tray which we lined with LDPE plastic that is typically used to wrap samples for trace metal analysis due to its low trace metal content.

Q. Line 151: Please provide the location from where the south Atlantic seawater sample was collected. R. Line 151: suggestion accepted, South Atlantic (40°S – it was filled pumping underway to keep the inflow clean and there is no fixed longitude, but the exercise was conducted offshore)

Q. Line 157: What was the duration for Mucosal stage? R. Line 157: Clarification made (3 days), now more details have been added to the text

Q. Lines 167 to 168: Replace “shaken by hand” with “manually shaken”. R. Lines 167 to 168: suggestion accepted.

Q. Line 167: Replace “into” with “to”. R. Line 167: suggestion accepted.

Q. Lines 174 to 175: How was the instrument calibrated. Could you please provide some more details? R. Lines 174 to 175: Standard additions of Fe(II) were used to

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calibrate the instrument, with peak height then used to derive Fe(II) concentration. Additional details are added (new lines 188-196).

Q. Line 175: Replace “dissolution” with “leaching”. R. Line 175: suggestion accepted.

Q. Line 179: Replace “dessert” with “desert”. R. Line 179: suggestion accepted.

Q. Line 183: Insert “major” before “ions”. R. Line 183: suggestion accepted.

Q. Line 184: This is the only place in the manuscript where any sample from the Aysén Fjord is mentioned. R. Line 184: A clarification is made why we used this water (to avoid using water which had already had a high ash load in our leach experiments)

Q. Lines 191 to 193: Rephrase as: “Samples were immediately analysed for total alkalinity (AT) via a potentiometric titration.”. R. Lines 191 to 193: suggestion accepted.

Q. Line 200: Please expand APHA. R. Line 200: APHA explanation extended. The full name: American Public Health Association, 2006.

Q. Lines 203 to 206: At what station/location were these measurements made? R. Lines 203 to 206: Clarification made. Time series is from the oceanographic buoy at the Reloncaví fjord.

Q. Line 204: How was the dissolved oxygen sensor calibrated? R. The sensor installed at the NPOB was factory calibrated and was a brand-new instrument when installed. Details are in Vergara-Jara et al., 2019.

Q. Line 230: Replace “onto” with “of sampled water through”. R. Line 230: suggestion accepted.

Q. Line 232: Replace “was” with “were”. R. Line 232: suggestion accepted.

Q. Line 247: Could you provide a reference for significant spread of 2015 Calbuco ash to Pacific and Atlantic regions. R. Line 247: Two important references have been added.

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Q. Line 269: Please provide the location of mooring station here. It has been mentioned later in line 311. R. Line 269: The Reloncaví fjord mooring is clearly label in Fig. 1 C. As North Patagonia Oceanographic Buoy.

Q. 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? R. Figure 4: There’s no clear reason on why station B at the center of the sampled locations got those values, but, it is not unusual to see patchiness in biological parameters (chla, or group distributions) along the fjord presumably due to local circulation patterns that can create zones with different resident time inside the fjord.

Q. 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. R. Lines 303 to 305: Correction made following suggestion. Peak was at stations A & C around May 16, and lower abundances was at station B (open circle) as well noticed by this reviewer.

Q. Figure 5: If discussing the brackish water leach experiments at first, place the results for brackish water on the left-hand side panel. R. Figure 5: The figure now shows the brackish water at left, and the scale has been fixed in order to show better the differences between the treatments.

Q. 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? R. Table 1: The fresh fjord brackish water used in the experiments has a relatively high background concentrations of macronutrients and major ions, so for major ions we present only results from DI water where it was possible to observe the increase from the ash leachate.

Q. Figure 6: One of the data points (on all plots) at high ash addition (between 5 and

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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. R. Figure 6: The vertical error bar shown is the estimation of the standard deviation as the figure legend explains. Horizontal bars reflect the small variation in ash mass between replicates. Ash was pre-weighed, and then following addition to the experimental solution the vials were re-weighed to determine the exact mass added to solution – static charges have resulted in a low, but varying, loss of sample during transfer, representing one of the challenges in working with small quantities under trace metal clean conditions.

Q. 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. R. Figure 6: The initial concentration was stated and we also stated that concentrations were presented as the change compared to initial concentrations in seawater. For clarity we add this information again (new lines 200-203).

Q. Lines 393 to 395: This is an important point, should have been brought out earlier. R. Lines 393 to 395: Note following more careful consideration that there is no clear decline in the Fe(II) released between 2 weeks and 4 months after collection, we have removed this section.

Q. 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)? R. Lines 496 to 497: Suggestions accepted, a new brief sentence has been added to the text in section 2.

Q. 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

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deposition over the region? R. Lines 575 to 577: This is certainly a possibility, although the peak in chlorophyll-a prior to the increase in UV aerosol index makes it difficult to ascribe the subsequent peak to ash fertilization. We have however now revised the manuscript to state:

Conversely, ash deposition into the south western Atlantic indicated by the UV aerosol index did not lead to such a clear corresponding change in chlorophyll-a concentrations (Fig. 8H), although with the available data it is not possible to rule out the possibility of fertilisation completely (e.g., whilst also being preceded by a larger chlorophyll-a peak on August 21st, there is a peak in chlorophyll-a at August 25th coincides with elevated UV aerosol index).

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