

# ***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.***

## **Anonymous Referee #3**

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### General Overview

The manuscript by Vergara-Jara et al addresses some important topics with respect to the influence of volcanic eruptions on marine productivity – notably the release of major ions and trace elements from ash deposited to surface waters and the range of possible biological responses to those inputs, based on biogeochemical conditions present at the time. The authors discuss results from a series of leaching experiments performed

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on ash from a 2015 eruption of the Calbuco volcano and combine this information with time-series data from the nearby Reloncavi Fjord to try and identify possible influence from ash inputs. They also use satellite data of ash dispersion from the eruption and marine chlorophyll-a concentrations to compare responses of ash inputs from the volcano to the eastern South Pacific and the western South Atlantic Oceans. Overall, I thought that the manuscript was well written and fairly concise, though there are places where it would benefit from a more in-depth discussion of the caveats associated with the data. The manuscript addresses phenomena that it is difficult to plan comprehensive studies of and could therefore be a useful addition to the literature on these topics. However, there are issues with the current version that need to be addressed before publication, which I will lay out below.

### Specific Comments

The ash sample was collected two weeks after the eruption and the meteorological data in Figure 3 indicates some rainfall (albeit in a different location to where the ash was collected) in the period between eruption and sample collection. Is it possible that the collected ash had been exposed to rainfall before collection? If so, can the authors discuss how this may have influenced their findings in terms of leachable trace elements and major ions?

There are numerous points to address with the methodology of the leaching experiments:

1) The leaching experiments conducted for determination of dissolved TMs into seawater, Fe(II) into seawater, and alkalinity and major ions into brackish and deionized water all use different experimental approaches, in terms of volumes used, ash loading, and length of mixing time. This is most relevant for the comparison of dissolved Fe versus Fe(II). While such differences in approach are sometimes unavoidable, the authors should at least discuss the potential for complications resulting from these differing approaches, particularly for the iron data – can they rule out any methodological

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artefacts in the data?

2) The method for the Fe(II) release leaching experiment states that subsamples were introduced into the flow-injection system without filtration. Does this not admit a potential positive bias in the released Fe(II) data through small ash particles getting trapped in the FIA manifold and undergoing further leaching and/or reaction with the FIA reagents?

3) In the Fe(II) method description it states that measurements were made every two minutes for 30 minutes for each ash loading, and that the data presented are “mean concentrations measured from 2-30 minutes after adding ash into solution”. Does this mean that all of the data from 2-minute intervals are averaged to produce the data points in Figure 7? Was there no significant temporal progression of concentration over this ~30-minute period? A related point is that if the data points in Figure 7 are mean values, presumably the standard deviations could be added to give a clearer idea of the significance of differences between datapoints.

4) Is there any scientific significance to the two ash size fractions chosen in the alkalinity/major ions leach experiments?

5) The description of dFe release in section 3.4 is described as being most efficient at the lowest ash loading per unit volume of seawater (line 351). Similarly, in Section 4.2, release of Fe and Mn is referred to in terms of nmol/g. This would be easier for the reader to visualize if Figure 6 was altered. Either additional plots could be included to plot each element as nmol/g released versus ash concentration in mg/L (as in Figure 7), or these plots could be superimposed on the existing plots by including secondary x- and y-axes.

6) For the Fe data in Figure 6, the value for the lowest ash addition has a large standard deviation. In Figure 7 we see that this is due to one replicate with a very high amount of Fe released per gram and two replicates with low values. The difference is very striking. Can the authors comment on the likelihood that the high value is an outlier

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and/or due to sample contamination? If not due to contamination, could this value be due to a methodological artefact?

7) At line 381 the release of Fe(II) from ash is referred to in terms of nmol/L, but Figure 7 does not show this as it relates to ash loading. It may be useful to include an additional panel in Figure 7 that shows the nM Fe(II) release as a function of ash added.

8) At line 393, the authors mention an apparent decrease in Fe(II) release with aging, but the only notable decrease seems to be between 4 months and 9 months, with little apparent difference between the trends at 2 weeks and 4 months. This should be clarified (e.g. “The release of Fe(II) from ash therefore appeared to decrease with aging after several months”).

Figure 4 – In section 3.2, this figure is used to make a comparison between diatom abundance at stations in the upper part of the fjord, and historical data from Reloncavi Sound, which presumably undergoes more circulation and has a shorter residence time for waters. In addition, the new data is integrated over the upper 15m, compared to the upper 10m for the literature data. The comparison is quite striking. I appreciate that there is a desire to put the new data into some kind of historical context, but I think the authors should include the caveat in section 3.2 that the new and historical datasets may not be directly comparable. The authors do state in the discussion that the data is not directly comparable to the historical data (lines 426-427), but I think this point also needs to be made in the results section.

Figure 8 – The apparent differing responses in the eastern Pacific and western Atlantic to ash deposition is a very interesting aspect of this study. However, I believe it would strengthen the findings of this paper if the authors could rule out the possibility that the observed response in chlorophyll in the Pacific Ocean is coincidental to the ash input. Figure 8G compares the satellite-derived aerosol index and chlorophyll-a concentration in the Pacific region over which the ash cloud passes. Have the authors looked at making a chlorophyll-a time-series at a similar area that did not see a strong variation

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in the aerosol index (for example, the area immediately to the south of the box used in 8G)? If no chlorophyll-a bloom corresponding to that in 8G is observed at this “no-ash” site, it would strengthen the argument that ash deposition was the trigger. Similarly, on the Atlantic side, there is a smaller ash-impacted area to the south of Rio de la Plata evident in panels C and D. Have the authors looked for any possible chlorophyll-a signal in that region and if they have, do the findings concur with the findings in panel H (i.e. that there is no ash-driven bloom)? Admittedly the aerosol index for this area looks substantially smaller, and cloud cover in the later time-period covered (panel F) may prevent a proper analysis of this area. Line 557 - The Browning et al (2015) reference suggests that in some cases, ash can bias satellite-derived chlorophyll-a measurements upwards significantly due to the optical properties of the ash and the algorithms used to convert data into chlorophyll concentrations. Can such a bias be ruled out in this study?

Technical comments:

Line 71 – no need for hyphen in micronutrient

Line 179 and throughout Supplementary Table 1 – replace “dessert” with “desert”.

Line 187 – “fresh water” – use deionized water throughout. There is potential for this to be confused with river water.

Line 194 – change to “a reproducibility of <2 umol/kg”

Lines 303-305/Figure 4 – It appears that the legend for Figure 4 is incorrect. It looks as though diatom abundance is greater at stations A and C, rather than B and C as stated in the text. The data in supplementary table 2 indicates that the figure is wrong, rather than the text. Based on the supplementary table, I would say that circles are station A, triangles are station B, and squares are station C.

Line 304 (and 431) – in both cases it is stated that diatom abundances were measured on 16th May, yet the supplementary table gives the date as 14th May. Which is it?

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Lines 305-307 – It would be more accurate to say that highest measured chlorophyll was on 30th April at a station close to station C. Based on Figure 4 it can't be said that concentrations decreased to much lower concentrations in June, as there isn't any data shown for June.

Line 339 – No need for “and” after NH<sub>4</sub>.

Table 1 – It states in the caption that all values are means. It would be more informative to also include standard deviations in the table if the data is from replicates – this would allow readers to assess whether changes observed with time are significant or due to noise in the measurements. Also, how is the detection limit arrived at? Is it 3x standard deviation of a blank?

Line 356 – I'm not convinced that Ni shows that trend – only two additions seem to give a positive increase in Ni concentration, with one of those being the highest ash loading, and this gives a false impression that there is a positive trend. I would group Ni with Cd rather than Co and Pb.

Figure 7 – The “ash 9 months” data does not match that in the supplementary table, in that in the table all four data points are between 18-31.9 mg/L. with corresponding nmol/g values of ~2 to ~16. Line 439 – change to “ash deposition per unit area”

Line 509/10 – It seems more appropriate here to refer to Figure 7 (right hand panel), as that shows the data in terms of nmol/g, as mentioned in the text, rather than the nmol/L change shown in Figure 6.

Line 549-550 – is there a possibility here that small particulates could have contributed to the Fe(II) concentrations (as these samples were not filtered between ash addition and analysis)? See specific comment earlier in review.

Line 605 – rather than “correlation”, which suggests a statistical relationship between the two parameters, I would suggest rephrasing this to something more general, such as “atmospheric ash loading was related to an increase in chlorophyll-a” (that is unless

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the authors can include a panel in figure 8 that does indeed show a correlation between satellite derived chl-a and aerosol index). Note also that the ash distribution shown by the aerosol index does not necessarily translate to “deposition” as stated here.

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