

## ***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. R replies.

Q. 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

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so, can the authors discuss how this may have influenced their findings in terms of leachable trace elements and major ions?

R. To Specific Comments: the ash sampled was collected after the third eruptive pulse and the collected ash was from a dry surface that was not rained before sampling. This was done to decrease the uncertainty of following leaching procedures.

Q. 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 artefacts in the data? R. 1) We did use different experimental approaches, but for different objectives and specific reasons. Regarding our most important finding on using fresh ash and the effect of Fe release, we did follow similar leaching protocols in order to avoid methodological artifacts of the data. The switch of method to a larger volume and colder temperature for Fe(II) measurements was done precisely to avoid artefacts in the Fe(II) data as at room temperature we would under-estimate any Fe(II) release, and with a low volume the constant removal of solution for flow injection analysis would potentially change the ash loading during the experiment. The specific potential issue with ash particles being measured as Fe(II) can be ruled out (see below) based on the absence of an increase in measured Fe(II) with increasing ash, and no detectable Fe(II) after experiments were conducted and blanks were run through the instrument.

Q. 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? R. 2) We tested for this, both the deionized water blanks run before/after

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loading (which were always below detection) and the absence of an increase in Fe(II) signal with increased ash loading suggested that there was no detectable effect associated with ash particles running through the apparatus either being detected as what we assume is dissolved Fe(II), or 'sticking' and causing an increased Fe(II) signal. We should also note that the FIA inflow was rigidly positioned at mid-depth in the incubation bottles used to prevent potentially large particle uptake if/when ash settled from suspension.

Q. 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. R. 3) Yes this is correct, and in hindsight we should have shown the temporal trend as this also provides some insight into the origin of this Fe(II) as discussed by reviewer 2. In order to discuss the time-series across all experiments together, we normalize each experiment (i.e. each ash incubation followed by >30 minutes of monitoring) to the median concentration of each individual time-series. The whole set of experiments can then be considered together, where 1.0 on the y axis corresponds to the median Fe(II) concentration observed, to see the general temporal trend (with standard deviations – these are not shown on the plot with all experiments for clarity).

Q. 4) Is there any scientific significance to the two ash size fractions chosen in the alkalinity/major ions leach experiments? R. 4) Yes, the two different ash size fractions were chosen to look at the effect of different particle size, as is known that leaching can vary drastically because smaller particle size has a much larger bigger surface for interactions related to its mass. Ultimately, based on the size fractions represented above,

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we tested both the dominant size fraction by mass (250-1000 um) and by surface area (<63 um), the latter proving an overwhelming contribution to leaching products as demonstrated here. The size fractions of the ash are now stated for clarity (lines 215-217).

Q. 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. R. 5) Yes, this is now provided in the supplement.

Q. 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 and/or due to sample contamination? If not due to contamination, could this value be due to a methodological artefact? R. 6) Yes, looking at all the trace elements, there are some triplicates with relatively large standard deviations. This is not unique to Fe, and is generally more common for low concentrations of Pb, Cd, Co and Ni. There are several contributing factors to this; the deduction of the initial concentration adds to the uncertainty especially when the net change after ash addition is low, for the lowest ash loadings the number of particles is low and therefore any therefore variability between replicates likely poorer. The highest of the dFe values could be labelled an outlier, but so could several of the other individual measurements if we look at all metals. Although blanks and replicate measurements were always ok, contamination of an odd value is always possible, but it is difficult to conclusively separate this from the inherent variability in metal composition when using small quantities of ash. This raises an important point which we now use to better separate the different metals into groups – that we

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should consider the measured change in solution relative to the background concentration and its variability (i.e. to the starting concentration and its standard deviation) as with some elements it is not possible to meaningfully discern trends from background variation.

Q. 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. R. 7) We can show the same data with different units, but prefer to do this in the supplement.

Q. 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"). R. 8) No longer in the manuscript following earlier comments about the temporal development of Fe(II) from another reviewer

Q. Comment on section 3.2 - 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 Reloncaví 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. R. Comment on section 3.2 - Figure 4.) Suggestion accepted. Now after the first sentence says "Historical data from González et al., (2010) is not directly comparable with recent data but gives a site-seasonal useful context." We calculate the potential difference in

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our data if it were integrated to a different depth (10 m or 15 m), the difference is about 20%.

Q. Comment on 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 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? R. Comment on Figure 8.) Browning et al. (2015) found that in very low chlorophyll-a cases, the presence of ash in seawater could bias satellite-detected chlorophyll-a concentrations upwards. This bias was found to strongly decrease with increasing chlorophyll-a, such that at concentrations  $>\sim 0.5\text{mg/m}^3$  the calculated impact was very small (Fig. 4b in Browning et al., 2015). Background chlorophyll-a concentrations in the targeted satellite study regions were at or above these levels, suggesting the deposited ash would have relatively limited impact on satellite-retrieved chlorophyll-a concentrations.

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We have now conducted a similar analysis for a control region of the Pacific and south of the Rio de la Plata.

"Experiments with ash suspensions have shown that ash loading has a restricted impact on satellite chlorophyll-a retrieval 6, therefore offering a means to assess the potential biological impact of the 2015 Calbuco eruption in offshore waters. We found evidence for fertilization of offshore Pacific seawaters in the studied area (Fig. 8). Following the eruption date, mean chlorophyll-a concentrations increased ~2.5 times over a broad region where elevated atmospheric aerosol loading was detected (Fig. 8G). Both the timing and location of this chlorophyll-a peak were consistent with ash fertilization, with the peak of elevated chlorophyll-a being located within the core of highest atmospheric aerosol loading, and the peak date occurring one day after the main passage of the atmospheric aerosol plume. A similar phytoplankton response timeframe was reported following ash deposition in the NE Pacific following the August 2008 Kasatochi eruption 7 which was similarly thought to be triggered by relief of Fe-limitation 8. At the same time, a control region to the south of the ash-impacted Pacific region showed no clear changes in chlorophyll-a matching that observed in the higher UV aerosol index region to the north.

A smaller ash impacted area to the south of the Rio de la Plata, where nitrate levels are expected to be higher than to the north, but with Fe levels also expected to be elevated due to its location on the continental shelf, showed a chlorophyll-a peak 7 days after the UV aerosol peak (Sup. Fig. 1). However, this was not well constrained due to poor satellite coverage in the period after the eruption. Considering the dynamic spatial and temporal variation in chlorophyll within this coastal area, it is challenging to associate any change in chlorophyll specifically with ash arrival."

Q. Line 71. No need for hyphen in micronutrient R. Line 71. Suggestion accepted.

Q. Line 179. and throughout Supplementary Table 1 – replace “dessert” with “desert”.  
R. Line 179. Suggestion accepted.

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

Q. Line 194. change to “a reproducibility of <2 umol/kg” R. Line 194. Suggestion accepted.

Q. 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. R. Lines 303 – 305. Suggestion accepted. Figure 4 it was showing incorrectly the stations diatom data. In old figure 4, circles were station A, triangles B, and squares C. New figure 4 has data corrected. Text was also modified in order to accurately show the changes (figure legend).

Q. 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? R. Line 304 and 431. Suggestion accepted. Measurements were made on 14th May, like the supplementary table show.

Q. 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. R. Lines 305-307. Suggestion accepted. Modified text now says: "Diatom abundance integrated to 15 m depth peaked at Stations A and C around 14th May, with notably lower abundances at the more freshwater influenced station B (Fig. 4), that is at middle point between all 3 major rivers. Highest measured Chlorophyll-a concentrations was on 30th April at Station C, including two nearby measurements from Yevenes et al., (2019), then chlorophyll-a values declined to much lower concentrations in late May which is expected from patterns in regional primary production (González

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et al., 2010)".

Q. Line 339. No need for "and" after NH4. R. Line 339. Suggestion accepted.

Q. 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? R. Note now Table 2. Please note also there were some unit errors in the data for the larger size fraction, the correct values are now shown (this does not change any trends or our interpretation). Literature values are also shown. SDs are quoted in addition to the means. Yes this is correct.

Q. 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. R. Line 356. We created a new grouping system for trace elements by first considering whether or not a trend could be discerned from background variability (i.e. is the change large compared to the mean and standard deviation of the starting water) and then considering the linearity of the trend with ash. A new paragraph is added (new lines 374-388).

Q. 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. R. Figure 7. Yes, there was an error in the table now corrected.

Q. Line 439 – change to "ash deposition per unit area" R. Line 439. Suggestion accepted.

Q. Lines 509 – 510. 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. R. Lines 509 – 510. The text here has changed

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following other comments.

Q. Lines 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. R. Lines 549 – 550. Not really, as we would expect to see an increase in Fe(II) with increasing ash load if that were the case. There was also no evidence for measurably increased Fe(II) from particles 'sticking' inside the apparatus (blanks before and after experiments were below detection). We expect, but cannot explicitly prove, that the measured Fe(II) is therefore dissolved.

Q. 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 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. R. Line 605. Suggestion accepted.

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