

***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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The manuscript presents the results of a study aimed at assessing the impact of ash deposition on marine primary productivity in Reloncaví fjord, Patagonia in the wake of the 2015 eruption of Calbuco volcano, Chile. The authors performed ash leaching experiments using deionised water and seawater, and measured the releases of Fe(II), total dissolved Fe and other trace metals, including Co, Ni, etc. They also report

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in situ measurements of diatom abundances in Reloncavi Fjord, and satellite-derived chlorophyll-a concentration for the ocean region (SE Pacific) affected by ash deposition. The main authors' conclusions are: (i) the increase in diatom abundance inferred to have occurred in the Reloncavi Fjord may relate to ash inputs, but other factors can also explain this observation; (ii) a short duration phytoplankton bloom in the SE Pacific which coincides in time and space with the ash cloud dispersion; (iii) a decrease with time in the Fe(II) (the most bioavailable iron redox species) release from ash, suggesting that "fresh" ash may act as a stronger source of Fe(II) than previously thought.

In my view the ms of Vergara-Jara et al. requires substantial work. I have found the ms disjointed and it is difficult to see a coherent story. It contains many vague statements that are not backed up by a careful analysis of the data. For example, the authors conclude that Fe(II) release decreases from dry ash samples over time ('aged ash') and emphasise that it is a key result of their study. However, this trend is not apparent from the dataset presented; Figure 7 shows that several measurements corresponding to different ash "ages" produce the same Fe(II) release. A more careful and quantitative analysis is required.

The study also includes measurements of other ash (Etna and Chaiten) and dust (Saharan dust, glacial flour, iceberg-borne particles) materials. The reason for selecting these samples is obscure if not random. The data acquired in relation to these samples are almost not used in the discussion.

While recent studies address the question of the solubility of Fe(II) and Fe(III) in volcanic ash (Maters et al., 2016; Maters et al., 2017), these are not used here. The authors also barely acknowledge previous works on metal release from ash (Hoffman et al, 2012 and subsequent studies), although this information could be used for comparison purposes. In general, a more careful analysis and use of the scientific literature on the subject is needed.

I also had some difficulties with the different methods utilised to assess the element re-

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lease from the ash and other airborne materials. The fresh and brackish water leaching experiments were carried out using two ash size fractions ( $< 63 \mu\text{m}$  and  $250\text{-}1000 \mu\text{m}$ ). What does justify the choice of the two size fractions, except perhaps the availability of sieves in the laboratory? How well these size fractions represent the actual ash deposits? What is the corresponding specific surface area of the ash particles in each size fraction? The leaching protocols differ between the different measured parameters. This does not allow the rigorous testing of potential relationships between different ash properties.

Overall, the ms suffers in places from gloss simplifications and insufficient use of the huge literature body existing on the processes controlling the solubility of Fe in airborne mineral particles. The discussion is wobbly and the authors jump to conclusions quickly, although the data do not clearly support them.

Section 4.1 “Local drivers of 2015 bloom dynamics in Reloncavi Fjord” is a list of the potential factors that could explain the observed bloom and this section could have been written up without any prior data. I do not think it adds any new knowledge that would contribute to improve our understanding of the potential impact of ash inputs to (marine) water bodies.

Attributing Fe release from ash exclusively to the presence of iron-bearing salts is misleading. Leaching and dissolution of the aluminosilicate glass and minerals contained in ash is also a source of Fe(II) and Fe(III) (see Maters et al., 2017; 2017 and other studies).

L39 – should be cloud not plume. Same applies throughout the ms

L48 F not FI but F. Same applies throughout the ms and tables

L50 “higher than usual” by how much? Two times? An order of magnitude? Outside the multiannual variability?

L52 You should be transparent in the abstract that this is highly speculative (since no

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other measures in the fjord point to a phytoplankton response to ash addition).

L62 How can a micromolar concentration of Fe(II) be released when above you say only nanomolar concentrations of Fe are released?

L64 This is not justified. First, you assume only Fe(II) is bioaccessible, and second, it is based on Fe(II) decreasing in aged ash which is not well supported by the data.

L67 meaning?

L77 2010 not 2013

L81 Why 'therefore'? The preceding sentence deals with a case that is not in a HNLC area of the ocean.

L94 Perhaps in fresh water but I imagine any shift in seawater pH is extremely transient and localised due to strong buffering!

L99 2010 not 2013

L148 Had the ash been rained on in the interval between the eruption and sampling?

L151 But South Atlantic seawater is presumably not HNLC water, so its properties might lead to findings here only relevant to ash input to the South Atlantic. For example, HNLC seawater might have different types/abundances of Fe-binding ligands.

L152 Is there a basis for this range? Does it mimic the Calbuco ash loading to the SW Atlantic and SE Pacific regions studied?

L167 Again, if South Atlantic seawater is not Fe-limited, then presumably measurements of Fe(II) concentrations in this water cannot be generalised to reflect Fe release behaviour from ash in Fe-limited seawater. For instance, different types/abundances of Fe-binding ligands in HNLC water might strongly influence dissolved Fe concentrations on ash input to seawater.

L168 Why is the ash loading concentration different than that used for the trace metals

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above?

L175 What 'dissolution experiments'? Do you mean ash leaching in seawater?

L179 Should be desert and please specify which, for consistency with specifying the ash source (Etna, Chaiten).

L180 Please specify sources

L183 Please revise heading - species responsible for alkalinity, ions, and nutrients are not mutually exclusive.

L184 I thought it was Reloncavi Fjord?

L187 Do you mean deionized water here? If so, please say this instead to avoid misinterpretation to mean environmental/fjord fresh water.

L188 0.18 g ash in 40 mL is 4.5 g/L or a 1:222 ash:water ratio. Where does this come from (it is not from Witham et al. 2005)?

L200 Were saturation indices calculated for all species in solution?

L222 This should come after 'at 3 depths'.

L328 Isn't it 4.5 g/L (0.18 g in 40 ml)?

L335 This is probably just a surface area effect (i.e. smaller size particles for the same mass of ash release correspondingly more ions due to the greater surface area in contact with solution)

L335 Leaching not dissolution.

L338 Because  $\text{CaSO}_4$  salts are not as soluble?

L350-352 I don't see support for this statement. From Figure 7 (right) showing all replicates, the couple of high Fe release values per unit ash mass seem like outliers. In fact two of the lowest ash loadings exhibit among the lowest Fe release per unit

mass.

L356 Be careful with these statements, there is a lot of overlap of error bars so any apparent increase may not be significant.

L370 Why this temperature and not room temperature, like the others?

L374 If not in the legend, at least here in the caption you should state what they are (desert dust, glacial flour, iceberg particles) etc.

L374-375 It seems that the two other volcanic ash (Etna, Chaiten) are included here to represent older ash samples, but if that's indeed the purpose, this is not a valid comparison because the different Fe chemistries (total Fe content, Fe redox speciation, and Fe mineralogy) in these samples are likely to be greater drivers of their Fe(II) release behaviours than the different ash ages. This must be acknowledged, or else I suggest removing the Etna and Chaiten ash from this study altogether.

L381 The Figure 7 y-axis reports Fe(II) release in nmol/g. Please be consistent for clarity.

L391 Perhaps only at low ash loadings, it's hard to say from the few data points for 9 month old ash. I would not consider this a clear trend at all, and in fact the Fe(II) release from 4 month old ash is often higher than from 2 week old ash at the same ash loading.

L393 This is not at all supported by the data shown in Figure 7 (left), see my comment above.

L397 Are you sure that this corresponds to volcanic ash and not to volcanic sulphate aerosol?

L511 Again, have you tested for saturation of Fe(II) (and other species) in your leachates? It would be useful to explore the possibility of secondary phase precipitation explaining decreasing dissolved Fe(II) with increasing ash loading.

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L512 Again, I don't see clear evidence for this statement in the data (e.g., Figure 7 right).

L520 Although this notion is propagated in the literature, there remains a paucity of evidence for Fe salts on ash surfaces! This section is missing important information on the forms of Fe (Fe(II) and Fe(III) in ash) - in aluminosilicate glass and mineral network and Fe(-Ti) oxide minerals. Will mislead readers to claim Fe salts are responsible again when we know that's not the case.

L522-524 No. Fast release of Fe(II) is more likely to originate from leaching of the aluminosilicate glass. Please do your homework (e.g., see Maters et al. 2016 and 2017 - those studies done at pH 1, 2 and 5 but are still relevant sources of info on the forms of Fe in ash and its release into solution)!

L525 See earlier comments, this statement is simply not well supported by the available data.

L527 There's no such thing as acidic surface coatings. The presence of any salts on ash surfaces is the end product of prior reaction between acids (H<sub>2</sub>SO<sub>4</sub>, HCl) and the aluminosilicate → neutralisation

L529 How would an acid-base reaction be responsible for Fe(II) conversion to Fe(III)? Presumably the Fe(II) at the ash surface has somehow been oxidised to Fe(III) during storage, or else made to be less mobile in some other way...

L530 Again, based on the fact that your data do not support the conclusion that aged ash releases less Fe(II), this statement should be removed. In any case, the term 'aged' in the mineral dust/glacial flour/volcanic ash community often refers to material that has interacted with other species during atmospheric transport ('aging'), if anything increasing Fe solubility and Fe(II) mobilisation over time (e.g., see Maters et al. 2016).

L532 This is true simply because we know that airborne material (dust, flour, ash) undergoes atmospheric processing, including exposure to inorganic and organic acids

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and cloud condensation and evaporation cycles, that is likely to modify the Fe solubility and speciation in the material before deposition to water bodies. Please acknowledge the huge body of literature in this area.

L536-544 All this should be removed because it surrounds a claim about aging/Fe(II) release that is not supported by the data here.

L552 What aerosols? Please specify since the Fe chemistry in different particulate materials can vary drastically.

L553 Specify Calbuco 2015 ash. Saying 'fresh volcanic ash' is a gross generalisation and completely neglects existing studies reporting variable Fe release from ash, including Fe(II) and Fe(III) release by ash from different eruptions - Maters et al. 2017. Okay that study done at low pH but it shows that Fe chemistry in ash is highly variable and likely plays an important role in Fe release from ash in solution.

L561 Please specify ash or particle, if that's indeed what the satellite detected. The term 'aerosol' in the volcanology context most often refers to sulphate aerosol.

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