Answers to Reviewer 1.

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) 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 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 authored 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 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 ask/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 um 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.

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.

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-

minning 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&iId=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 (40ºS – 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 Mucasol 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 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.

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 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 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 proceeded 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).

Answers to reviewer 2 -Pierre Delmelle

Q. 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.

R. For the Fe(II) concentrations, because of the parametric fit to these data to ash loading and the fact they weren't collected specifically to test aging (we noticed afterwards there may have been some decline) with replicates of the exact same loading, it is difficult to show if there is a trend, especially since we agree that there is no clear change between the first two time points. This being the case we have removed comments concerning the potential decline from the manuscript.

Q. 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.

R. We simply wanted to test if other particles also released Fe(II) upon addition to seawater as there is sparse literature specifically testing this and so tested a broad range of particles from well characterized materials we have in our collection. However, as these are all aged, we agree the comparison is not particularly useful so have removed these parts of the manuscript.

Q. The fresh and brackish water leaching experiments were carried out using two ash size fractions (< 63 _m and 250-1000 _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.

R. We have included a new table that summarize all the leaching experiments done in this research, the analysis, the water used for the leachates, etc. In order to better explain the different methods used. The leaching protocols had to differ to make some measurements e.g. measurements of major ions in saline waters would not be possible due to the high background level of most ions, measurement of Fe(II) is not meaningfully possible at room temperature etc.

The size fractions used were selected to test the effect from different particle size. The corresponding size fractions used and their respective percentages from the total of the sample are: > 2360 um (4.54%); < 2360 um & >1000 um (6.85%); <1000um & >250um (31.12%); <250um & >125um (24.14%); <125um & >63um (18.04); <63um (15.31%). This information in now also included (new lines 215-217).

The main constraint on the selection of ash size fractions was the total mass of unhydrated ash available for experimentation, which generally is very limited for any given study and in our case precludes the robust testing of all possible experimental treatments. We therefore focused on the most meaningful treatments: major ions and macronutrients are effectively undetectable in given background levels in brackish or seawater matrices, and Fe is probably not a significant factor in terms of biogeochemical effects in freshwater systems. Particle size distributions generally vary considerably over the extent of ash plumes (and to some extent over short time scales), hence there is no standard "actual ash deposits" but a range, which for this event has not been to our knowledge characterized. The size fractions reported here are standard sieve sizes, their relation to previous studies is discussed above and they were selected as fractions which could be sieved and still produce enough material to work with (larger, or smaller, sieves would have not yielded enough material to conduct the work described herein from our bulk ash sample). Although the surface area was not estimated, based on previous studies (Brantley et al 1999 and Gauttier et al 2001, op cit. Jones and Gislason 2008), specific surface area will approximately double for each increment in smaller grain size (again based on standard 500, 250, 125, 63 µm series). Ultimately, based on the size fractions represented above, 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.

Q. 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.

R. We have carried out extensive modifications to remediate the gloss simplifications and insufficient use of the huge literature body, following the suggestions from all reviewers particularly removing the material which speculated a decline in Fe(II) release with aging. We focus on the novel aspects, which as commented by other reviewers, concern the Fe(II) release which has been poorly investigated into seawater.

Q. Section 4.1 "Local drivers of 2015 bloom dynamics in Reloncaví 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.

R. Section 4.1 is a section that was written thanks to the extensive and exhaustive environmental data gathered in this environment. To our knowledge similar biochemical in situ monitoring datasets are not present in the literature that have fortuitously measured, with high time resolutions (h), the potential effect of a volcanic eruption within an environment of similar characteristics like the Reloncaví fjord. We believe that having the possibility to measure the in situ data of a natural water body should be of interest for different scientific disciplines. We acknowledge that there does not appear to have been dramatic changes in the fjord and thus our summary of the shifts observed- which appear to be largely seasonal and not specifically in response to the ash deposition- is not particularly exciting, but this can only be concluded having seen the data.

Q. 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).

R. We have studied the literature concerning the evidence for iron-bearing salts and agree the evidence for this, whilst multi-faceted, is not entirely conclusive. However, our main line of argument, which was not developed previously, is the temporal development of Fe(II) during the leach experiments. This does show a pulse of Fe(II) released in the first minute of dissolution followed by a closer to steady-state situation later.

The studies quoted demonstrate leaching of Fe(II) at low pH. This is not comparable to work conducted in seawater, because the fraction of dFe leached as Fe(II) is sensitive to the solution pH and shows a non-linear relationship with pH (the ferrozine method used to quantify Fe(II) in the above studies is also prone to artefacts under low pH conditions). Similarly, the stability of Fe(II) in solution is highly dependent on pH. Experiments demonstrating that Fe(II) is leached under acidic conditions cannot therefore be used to extrapolate to seawater either from a concentration, or from a mechanistic perspective.

There are numerous papers providing varying lines of evidence for the release of Fe-bearing salts dominating dFe release over short (minutes) time periods. We accept however that these are not conclusive that this is the only source of dFe (or specifically Fe(II)). Following comments from another reviewer, we also now display the Fe(II) data from ash release as a time series (after ash addition to seawater). The temporal trend suggests that much of the Fe(II) is released in the first minute following addition to seawater suggesting that the origin of this Fe(II) is a highly soluble phase. We have amended the section accordingly (new lines 562-574).

Q. Line 39: should be cloud not plume. Same applies throughout the ms
R. Line 39: We refer to plume, because is from the eruption itself, while an ash cloud could form afterward from resuspension of old ash deposits. The ash studied here came from the eruption plume. Ash cloud is used in the context of the satellite analyses.

Q. Line 48: F not Fl but F. Same applies throughout the ms and tables
R. Line 48: Correction accepted. Changed all throughout the ms.

Q. Line: 50 “higher than usual” by how much? Two times? An order of magnitude? Outside the multiannual variability?
R. Line 50: About two times and up to four times higher (Gonzalez et al 2010; Montero et al., 2011) for corresponding season, Autumn).

Q. Line 52: You should be transparent in the abstract that this is highly speculative (since no other measures in the fjord point to a phytoplankton response to ash addition).
R. Line 52: We change the phrase to: Within Reloncaví Fjord, average integrated peak diatom abundances were higher than usual by up to two times (May diatom abundance cell*10^9 m-2), integrated to 15 m depth), with the bloom intensity perhaps moderated due to high ash loadings in the weeks following eruption.

Q. Line 62: How can a micromolar concentration of Fe(II) be released when above you say only nanomolar concentrations of Fe are released?
R. Line 62: Note the units are different “nmol l^{-1}“ refers to the Fe concentration in solution. “µmol g^{-1}“ refers to the Fe in solution per unit of ash. The units/values are correct as stated.

Q. Line 64: 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.
R. Line 64: This is based on the observation that Fe(II) was released, not on how it aged. A room temperature leach with subsequent measurement of dFe would not detect this Fe(II), it would already have re-oxidised and precipitated as Fe(III) before it could even be filtered and preserved. We are not assuming Fe(II) is bioaccessible, or that only Fe(II) is bioaccessible. Irrespective of whether Fe(II) is bioaccessible or not, increasing its concentration increases the bioavailable pool of Fe by maintaining a higher concentration of Fe in the dissolved phase which can be (and is) actively cycled via Fe(III) phases.

Q. Line 67: Meaning…
R. Line 67: We just wanted to frame this in an environmental context, this is a high fraction relative to what you can observe in the natural environment (much higher, for example, than the ratio in bulk seawater and comparable to that observed in a highly-photochemically affected context).

Q. Line 77: 2010 not 2013
R. Line 77: change done, 2010.

Q. Line 81: Why ’therefore’? The preceding sentence deals with a case that is not in a HNLC area of the ocean.
R. Line 81: Sentence changed to another connector.

Q. Line 94: Perhaps in fresh water but I imagine any shift in seawater pH is extremely transient and localised due to strong buffering!
R. Line 94. Yes, clarified, although the fjord surface layer is relatively fresh and thus more weakly buffered.

Q. Line 99: 2010 not 2013.
R. Line 99: change done.

Q. Line 148: Had the ash been rained on in the interval between the eruption and sampling?
R. Line 148: No, the ash was gathered from fresh deposition at the eruption nearby area, from ash than had been falling down on the day before.

Q. Line 151: 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.
R. Line 151: Yes, in short, the exact seawater used will have several influences on the Fe leached from ash int solution. Ligand concentration being one of them. This affects any leach experiment and is not specific to the work herein. S Atlantic water with a relatively typical dFe starting concentration was used as the most representative seawater supply we could access.

Q. Line 152: Is there a basis for this range? Does it mimic the Calbuco ash loading to the SW Atlantic and SE Pacific regions studied?
R. Line 152: As we don't have data about the natural ash loading at the ocean regions studied here after the Calbuco eruption, we can't answer this question. The ash loadings are designed to be broadly comparable to the range used in prior work. There is no clear reason to choose a specific loading, as the loading gradient in any eruption is always very broad both spatially and temporally.

Q. Line 167: 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 HLNC water might strongly influence dissolved Fe concentrations on ash input to seawater.
R. Line 167: It's not clear what the reviewer means here, there is no such thing as Fe-limited seawater, Fe-limited refers to phytoplankton status. The ratio of dFe:macronutrients could be used to indicate if seawater is deficient. Generally higher ambient dFe concentrations (i.e. non-dFe-deficient conditions) would lead to saturation more easily, so the Fe-leached from ash would be potentially reduced compared to starting with lower ambient dFe concentrations. With respect to ligands, 'Fe-binding ligands' almost invariably refers to Fe(III)-binding ligands[5], the effect of which would not be direct on short-term (seconds-1 minute) Fe(II) release into solution. Fe(II)-binding ligands may exist in an environmental context, but they are not thought to compose such a large influence on Fe(II) speciation as Fe(II) is a transient specie the distribution and concentration of which is dominated by redox dynamics rather than by ligand properties.

Q. Line 168: Why is the ash loading concentration different than that used for the trace metals above?
R. Line 168: because these are two different experiments. For Fe(II), we noticed that there was pronounced sensitivity to the ash loading, so expanded the range of conditions to see what the very high/low loading/Fe(II) release looked like.

Q. Line 175: What 'dissolution experiments'? Do you mean ash leaching in seawater?
R. Line 175: Yes.

Q. Line 179: Should be desert and please specify which, for consistency with specifying the ash source (Etna, Chaiten).
R. Line 179: No longer present in manuscript.

Q. Line 180: Please specify sources
R. Line 180: No longer present in manuscript.

Q. Line 183: Please revise heading - species responsible for alkalinity, ions, and nutrients are not mutually exclusive.
R. Line 183: heading of point 2.3 changed to: 2.3 Ash samples – DI and brackish leaching experiments.

Q. Line 184: I thought it was Reloncavi Fjord?
R. Line 184: This was the fieldsite. But consider that this fieldsite had experienced a huge deposition of ash, we suspected that collecting water which already had experienced a large ash exposure (and at the time of our ash collection still had a visibly high ash loading) would not be particularly insightful for leach experiments. We therefore collected water from an adjacent fjord to conducted our leaching experiments with.

Q. Line 187: Do you mean deionized water here? If so, please say this instead to avoid misinterpretation to mean environmental/fjord fresh water.
R. Line 187: Suggestion accepted, now says DI water.

Q. Line 188: 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)?
R. Line 188: The total amount of that sample was divided in order to have a good number of replicates. Following most of Witham et al., (2005) recommendations, point 5: 1; 2; 3; 4; 8 and 9. 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, considering the total flow through their reactor. Finally, it’s the time scales that are probably most relevant, together with the selection of the finest size fraction.

Q. Line 200: Were saturation indices calculated for all species in solution?
R. Line200: We ran Visual MINTEQ 3.1 for average the ionic composition of the 63 um size fraction (which had the highest yield of leachates) together with three scenarios of pH (5, 6 and 7) and Fe (4.5) – note that since these parameters were not measured for the freshwater experiments they are merely parameterized here based on plausible values (e.g. Fe should be within an order of magnitude of marine leaching following the results shown in Jones and Gislason 2008). The results are included in the Supplementary material, and show highly undersaturated conditions for almost all potential minerals except for iron hydroxide species.

Q. Line 222: This should come after “at 3 depths”.
R. Line 222: Suggestion accepted.

Q. Line 328: Isn’t it 4.5 g/L (0.18 g in 40 ml)?
R. Line 328: Suggestion accepted.

Q. Line 335: 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). Leaching not dissolution.
R. Line 335: Suggestion accepted.

Q. Line 338: Because CaSO4 salts are not as soluble?
R. Line 338: CaSO4 salts are secondary minerals, among an array of species that are, according to the charge balance and the results from various time steps, far from equilibrium.

Q. Lines 350-352: 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.
R. Lines 350-352: Following comments from another reviewer, we have better grouped the behavior of the metals considering the quality of the fit over the applied ash gradient, and the magnitude of the change in concentration compared to the initial concentrations. New lines 379-388 are therefore re-written, and p values are added to new Figure 6.

Q. Line 356: Be careful with these statements, there is a lot of overlap of error bars so any apparent increase may not be significant.
R. Line 356: Suggestion accepted. We have added regression fits and p values to the plots showing changes in trace metal concentration with time. We also discuss which elements we cannot discuss meaningfully due to the limited change compared to background concentrations. We have modified this discussion to exclude elements where we cannot meaningfully determine trends (new lines 379-388).

Q. Line 370: Why this temperature and not room temperature, like the others?
R. Line 370: Fe(II) is unstable at room temperature under oxic conditions (now explained in the text).

Q. Line 374: If not in the legend, at least here in the caption you should state what they are (desert dust, glacial flour, iceberg particles) etc.
R. Line 374: No longer in manuscript following earlier comments.

Q. Lines 374 - 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.
R. Lines 374 - 375: No longer in manuscript following earlier comments.

Q. Line 381: The Figure 7 y-axis reports Fe(II) release in nmol/g. Please be consistent for clarity.
R. Line 381: We have shown the Fe(II) results as nmol g^{-1} in figure 7 because of the sharp curve that results, in Figure 6 we plot the concentration as nM because the propagated error on nmol g^{-1} becomes huge for those elements that do not show a pronounced change. As the

data displayed as nmol g^{-1} was however also requested by another reviewer, we add it in the supplement.

Q. Line 391: 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.
R. Line 391: No longer in manuscript following earlier comments.

Q. Line 393: This is not at all supported by the data shown in Figure 7 (left), see my comment above.
R. Line 393: No longer in manuscript following earlier comments.

Q. Line 397: Are you sure that this corresponds to volcanic ash and not to volcanic sulphate aerosol?
R. Line 397: The UV Aerosol Index largely reflects the strongly UV-absorbing (dust) aerosols. Sulphates are weakly/non-absorbing aerosols and therefore thought to have a more restricted contribution to the absorption signal.
Reference:
Torres, O., Tanskanen, A., Veihelmann, B., Ahn, C., Braak, R., Bhartia, P.K., Veefkind, P. and Levelt, P., 2007. Aerosols and surface UV products from Ozone Monitoring Instrument observations: An overview. Journal of Geophysical Research: Atmospheres, 112(D24).

Q. Line 511: 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.
R. Line 511: (Saturation is tested for in the Supplement). Specifically for Fe(II), Fe(II) is inherently unstable under these conditions, decaying on a timescale of minutes even with the reduced temperature. It therefore doesn't really make sense to us to consider the extent to which Fe(II) is saturated in solution. With respect to dFe, these concentrations are likely over-saturated as ligand concentrations in this same S Atlantic water have previously been determined to be about 1.5 nM.

Q. Line 512: Again, I don't see clear evidence for this statement in the data (e.g., Figure 7 right).
R. Line 512: Please see comment above for line 393. We have re-written this section.

Q. Line 520: 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.
R. Line 520: As per above comment. Our Fe(II) vs time plots show relatively unambiguously that there was a sudden pulse of Fe(II) release into solution occurring between 0-60 s after ash addition. We do not think that the shape of the Fe(II) vs time plot is not consistent with leaching from a solid aluminosilicate glass phase and suspect it is more consistent with a sudden dissolution effect. However we recognize this is not unambiguous and accordingly have rewritten (new lines 562-574)

Q. Lines 522 – 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)!
R. Lines 522 – 524: These leaches in acid cannot be extrapolated to seawater at pH 8 (see earlier comment). If it were the case that Fe(II) were released from a mineral phase, we do not think that this would produce the Fe(II) vs time distribution that we observed during the Fe(II) incubation experiments.

Q. Line 525: See earlier comments, this statement is simply not well supported by the available data.
R. Line 525: No longer in the text following earlier comments.

Q. Line 527: 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_2SO_4, HCl) and the aluminosilicate –> neutralization.
R. Line 527: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

Q. Line 529: 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...
R. Line 529: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

Q. Line 530: 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).
R. Line 530: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

Q. Line 532: This is true simply because we know that airborne material (dust, flour, ash) undergoes atmospheric processing, including exposure to inorganic and organic acids 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.
R. Line 532: we believe that in this statement the reviewer is referring to airborne material that has undergo atmospheric processing due to long transport time-distance. Here we worked with fresh ash that was deposited in the nearby volcano area shortly after its release, thus we are not concerned with processes occurring in the atmosphere days to months after an eruption. We were referring specifically to a method artefact – when conducting a dFe leach at room temperature, any Fe(II) released (or at least a substantial fraction of it) will precipitate before it can be measured as dFe using standard leaching techniques.

Q. Lines 536 – 544: All this should be removed because it surrounds a claim about aging/Fe(II) release that is not supported by the data here.
R. Lines 534 – 544: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

Q. Line 552: What aerosols? Please specify since the Fe chemistry in different particulate materials can vary drastically.
R. Line 552: The chemistry of these aerosols was highly variable as it refers to a transect over a large area of the offshore Pacific (we clarify the wording in the text "from aerosols collected across zonal transects of the Pacific Ocean"

Q. Line 553: Specify Calbuco 2015 ash. Saying 'fresh volcanic ash' is a gross generalization 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.
R. Line 553: Changed to 'Calbuco' as suggested.

Q. Line 561: 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.
R. line 561: For clarity we have replaced 'atmospheric aerosol loading' with 'UV aerosol index'

Answers to Anonymous Referee #3

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 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 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, 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 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 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 >~0.5mg/m3 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.

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 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.

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 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. SDs are now included, yes this is how the detection limit is defined. (Note, now Table 2)

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 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.

A mosaic of phytoplankton responses across Patagonia, the southeast~~SE~~ Pacific and southwest~~SW~~ Atlantic Oceans to ash deposition and trace metal release from the Calbuco ~~2015~~ volcanic eruption in 2015

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Key words: volcanic ash, iron, Fe(II), phytoplankton, carbonate chemistry, Reloncaví Fjord

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Abstract

Following the ~~April 2015~~ eruption of the Calbuco volcano in April 2015, an extensive ash plume spread across northern Patagonia and into the southeast~~SE~~ Pacific and southwest~~SW~~ Atlantic Oceans. Here we report on~~the results of~~ field surveys conducted in the coastal~~marine~~ region receiving the highest ash load following the eruption (Reloncaví Fjord). The fortuitous location of a long-term monitoring station in Reloncaví Fjord provided data to evaluate inshore phytoplankton bloom dynamics and carbonate chemistry during April-May 2015. Satellite derived chlorophyll-a measurements over the ocean regions affected by the ash plume in May 2015 were obtained to determine the spatial-temporal gradients in offshore phytoplankton response to ash. Additionally, leaching experiments were performed to quantify the release from ash into solution of total alkalinity, trace elements (dissolved Fe, Mn, Pb, Co, Cu, Ni and Cd) and major ions (Fl$^-$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, Li$^+$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}) ~~from ash into solution~~. Within Reloncaví Fjord, integrated peak diatom abundances during the May 2015 austral bloom were higher than usual (up to 1.4×10^{11} cells m^{-2}, integrated to 15 m depth), with the bloom intensity perhaps moderated due to high ash loadings in the two weeks following the eruption. Any mechanistic link between ash deposition and the Reloncaví diatom bloom can however only be speculated on due to the

lack of data immediately preceding and following the eruption. In the offshore southeast~~SE~~ Pacific, a short duration phytoplankton bloom corresponded closely in space and time to the maximum observed ash plume, potentially in response to Fe-fertilization of a region where phytoplankton growth is typically Fe-limited at this time of year. Conversely, no clear fertilization on the same time-scale was found in the area subject to an ash plume over the southwest~~SW~~ Atlantic where the availability of fixed nitrogen is thought to limit phytoplankton growth. This~~which~~ was consistent with no significant release of fixed nitrogen (NO_x or NH_4) from the ash.

In addition to release of nanomolar concentrations of dissolved Fe from ash suspended in seawater, it was observed that low loadings (< 5 mg L^{-1}) of~~ freshly deposited~~ ash were an unusually prolific source of Fe(II) into chilled seawater~~solution~~ (up to 1.0 µmol Fe g^{-1}), producing a pulse of Fe(II) typically released mainly during the first minute after addition to seawater. This release would not be detected, either as Fe(II) or dissolved Fe, following standard leaching protocols at room temperature~~suggesting that the release of bioaccessible Fe from ash sources may generally be under-estimated when quantified from aged ash, even from the same sample stored a few weeks~~. ~~-~~A pulse of~~This release of~~ Fe(II) release upon addition of Calbuco ash to seawater~~may~~ made it an~~make freshly deposited ash an~~ unusually efficient dissolved Fe source with the ~18-38% fraction of dissolved Fe released as Fe(II) from Calbuco ash roughly comparable to literature values for Fe released into seawater from aerosols collected over the Pacific Ocean which have been substantially moderated by photochemical processing.

1. Introduction

Volcanic ash has long been considered a large, intermittent source of trace metals to the ocean (Frogner et al., 2001; Sarmiento, 1993; Watson, 1997) and its deposition is now deemed a sporadic generally low ~~-~~macronutrient, high~~-~~ micro~~-~~nutrient supply mechanism (Ayris and Delmelle, 2012; Jones and Gislason, 2008; Lin et al., 2011). As volcanic ash can be a regionally significant source of allochthonous inorganic material to affected water bodies, volcanic eruptions have the potential to dramatically change light availability, the carbonate system, properties of sinking particles and ecosystem dynamics~~ in impacted waterbodies~~ (Hoffmann et al., 2012; Newcomb and Flagg, 1983; Stewart et al., 2006). Surveys directly underneath the ash plume from the 2013 eruption of Eyjafjallajökull (Iceland) over the North Atlantic found, among other biogeochemical perturbations, high dissolved Fe (dFe) concentrations of up to 10 nM in affected surface seawater (Achterberg et al., 2013) which could potentially result in enhanced primary production. The greatest potential positive effect of ash deposition on marine productivity would~~ therefore~~ generally be expected in high-nitrate, low-chlorophyll (HNLC) areas of the ocean (Hamme et al., 2010; Mélançon et al., 2014), where low Fe concentrations are a major factor limiting primary production (Martin et al., 1990; Moore et al., 2013). Special interest is therefore placed on the ability of volcanic ash to release dFe, and other bio-essential trace metals such as Mn (Achterberg et al., 2013; Browning et al., 2014a; Hoffmann et al., 2012), into seawater. ~~Conversely~~In contrast, apart from inducing light limitation, ~~other ~~there are several adverse effects of ash deposition on aquatic~~marine~~ organisms. These include~~ that go from~~~~negative effects of ash deposition on marine organisms could arise from~~ metal toxicity (Ermolin et al., 2018),~~-~~ particularly ~~when~~ under high dust loading ~~is high ~~(Hoffmann et al., 2012), and ~~- or more generally from ~~the ingestion of ash particles by filter feeders, phagotrophic organisms or fish (Newcomb and

Flagg, 1983; Wolinski et al., 2013). Transient shifts to low pH have also been reported in some, but not all, ash leaching experiments and in some fresh~~some natural~~ waterbodies following intense ash falls, suggesting that significant ash deposition on weakly buffered aquatic environments can also impact and perturb their carbonate system~~that perturbations to the carbonate system are a further impact of volcanic ash in aquatic environments~~ (Duggen et al., 2010; Jones and Gislason, 2008; Newcomb and Flagg, 1983). The greatest negative impact of ash on primary producers would therefore be expected closest to the source where the ash loading is highest and in areas where ~~abundance of~~ macronutrients or light, rather than trace elements, limit primary production.

In contrast to the North Atlantic 2013 Eyjafjallajökull plume over the North Atlantic, the 2015 ash plume over the region from the Calbuco eruption (northern Patagonia, Chile) was predominantly deposited largely over an inshore and coastal region (Romero et al., 2016) (Fig. 1). This led to visible high ash loadings in affected surface waters in the weeks after the eruption (Fig. 2), providing a case study for a concentrated ash deposition event in a coastal system; Reloncaví Fjord, which is the northernmost fjord of Patagonia. It receives the direct discharge ~~of~~ from three major rivers, creating a highly stratified and productive fjord system in terms of both phytoplankton biomass and aquaculture production of mussels (González et al., 2010; Molinet et al., 2017; Yevenes et al., 2019). Here we combine in situ observations from moored arrays which were fortuitously deployed in Reloncaví Fjord (Vergara-Jara et al., 2019), with satellite-derived chlorophyll data for offshore regions subject to ash deposition, and leaching experiments to investigate the inorganic consequences of ash addition to solution. We thereby evaluate the potential positive and negative effects of ash from the 2015 Calbuco eruption on marine primary production in three geographical regions;

Reloncaví Fjord and the areas of the SE Pacific and SW Atlantic Oceans beneath the most intense ash plume.

2. **Materials and methods**

2.1. *Study area*

The Calbuco volcano (Fig. 1) is located in a region with large freshwater reservoirs and a major river (the Petrohué) that flows into Reloncaví Fjord. The predominant bedrock type is andesite (López-Escobar et al., 1995). Reloncaví Fjord is 55 km long and receives freshwater from 3 main rivers, the Puelo, Petrohué, ~~Cochamó~~ and ~~Puelo~~Cochamó,~~,~~ with mean ~~monthly~~ stream flows of 650 m^3 s^{-1}, 350 m^3 s^{-1}~~,~~ and 100 m^3 s^{-1}~~,~~ ~~and 650 m^3 s^{-1},~~ respectively (León-Muñoz et al., 2013). River discharge strongly influences seasonal patterns of primary production across the region, supplying silicic acid and strongly stratifying the water column (Castillo et al., 2016; González et al., 2010; Torres et al., 2014). Seasonal changes in light availability rather than macronutrient supply are thought to control marine primary production across the Reloncaví region with high marine primary production ~~high~~ (>1 g C m^{-2} day^{-1}) throughout austral spring, summer and early autumn (González et al., 2010).

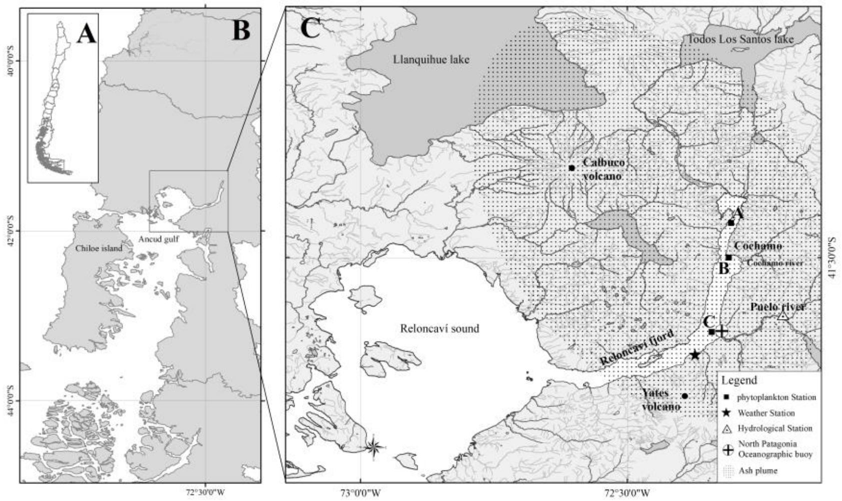

Figure 1. The Calbuco region showing the location of Reloncaví Fjord, 3 major rivers (Petrohué, Cochamó and Puelo) discharging into the fjord, the 3 stations (black squares; A, B and C) used to assess changes in phytoplankton abundance following the eruption, a hydrological station that monitors Puelo river flow, a weather station and the location of a long-term mooring within the fjord. The extent of the ash plume in the week following the eruption is illustrated, as estimated in technical reports issued by the Servicio Nacional de Geología y Minería.

On 22 April 2015 the Calbuco volcano erupted after 54 years of dormancy. Two major eruption pulses lasted <2 hours on 22 April and 6 hours on 23 April, releasing a total volume of 0.27 km^3 ash which was projected up to 20 km height above sea level (Van Eaton et al., 2016; Romero et al., 2016). Ash layers of several cm thick were deposited mainly to the NE of the volcano in subsequent days (Romero et al., 2016). Fortuitously, as part of a long-term deployment, an ocean acidification buoy in the middle of Reloncaví Fjord (Vergara-Jara et al., 2019) and an associated meteorological station close to the volcano (Fig. 1) were well placed to assess the impact of ash fall immediately after the eruption. To compliment data from these facilities, after the regional evacuation order was removed, weekly sampling campaigns were conducted in the fjord commencing one week after the eruption. The Chilean Geological-mining Survey (Servicio Nacional de Geología y Minería, SERNAGEOMIN) produced~~elaborated~~ daily technical reports including~~with information about~~ the estimated area of ash dispersion~~n for the emitted ash~~ (http://sitiohistorico.sernageomin.cl/volcan.php?pagina=4&iId=3). ~~We used~~ T~~t~~his information was used to create a reference aerial extent of ash deposition for the week~~days~~ after the eruption (Fig. 1, C).

2.2. Ash samples – trace metal leaching experiments

Ash (500 g) was collected (6 May 2015, in Cochamó, Chile) ~~from the surface of a plastic container (lid of a storage bin, 40 x 94 cm)~~ using a plastic tray wrapped with plastic sheeting (40 × 94 cm), double sealed in low density polyethylene (LDPE) plastic bags and stored in the dark. Ambient weather in the day preceding ash collection was dry. A sub-sample was analyzed for particle size using a Mastersizer 2000 at The University of Chile. Offshore~~South Atlantic~~ ~~(XX.XºS: XX.X º W)~~ seawater for incubation experiments was collected in the mid-South Atlantic (40° S) using a towfish and trace metal clean tubing in a 1 m^3 high density polyethylene tank which had been pre-rinsed with 1 M HCl. This water was stored in the dark for >12 months prior to use in leaching experiments. All labware for trace metal leaching experiments was pre-cleaned with Mucasol and 1 M HCl. 125 ml LDPE bottles (Nalgene) for trace metal leach experiments were pre-cleaned using a 3-stage procedure with three de-ionized water (Milli-Q, Millipore, conductivity 18.2 MΩ cm^{-1}) rinses after each stage (3 days in Mucasol, 1 week in 1 M HCl, 1 week in 1 M HNO_3).

Leach experiments were conducted by adding a pre-weighed mass of ash into 100 ml South Atlantic Seawater, gently mixing the suspension for 10 minutes, and then syringe filtering the suspension (0.2 µm, polyvinylidene fluoride, Millipore). Eight different ash loadings from 2-50 mg L^{-1} were used, with each treatment run in triplicate. Samples for dissolved trace metals (Fe, Cd, Pb, Ni, Cu, Co and Mn) were acidified within 1 day of collection by the addition of 140 µL HCl (UPA grade, ROMIL) and analysed by inductively coupled plasma mass spectroscopy following preconcentration exactly as per Rapp et al., (2017).

Leach experiments specifically to measure Fe(II) release were conducted in a similar manner but in cold seawater due to the rapid oxidation rate of Fe(II) at room temperature (~21°C), which makes accurate measurement of Fe(II) concentrations challenging (Millero et al., 1987). A pre-weighed mass of ash was added ~~in~~to 250 ml South Atlantic seawater and manually shaken ~~by hand~~ for approximately one minute. Ash loadings ranged from 0.2-4000 mg L^{-1}. Fe(II) was ~~then~~ measured via flow injection analysis using luminol chemiluminescence (Jones et al., 2013) without pre-concentration or filtration. The inflow line feeding the flow injection apparatus was positioned inside the ash suspension immediately after mixing and measurements begun thereafter at 2 minutes resolution. Reported ~~values are the~~ mean values (± standard deviation) are determined from the Fe(II) concentrations measured ~~from~~ 2-30 minutes after adding ash into solution. Calibrations ~~(Jones et al., 2013)~~ were run daily using standard additions of 0.2-10 nM Fe(II) to aged (unfiltered) South Atlantic seawater with integrated peak area used to construct calibration curves. Following each~~After~~ ~~dissolution~~ leaching experiment~~s~~ the apparatus was rinsed with 0.1 M HCl (reagent grade) followed by flushing with de-ionized water to ensure the removal of ash particles. Blank measurements before/after Fe(II) measurements from experiments with different ash loadings verified that there was no discernable interference from ash particles in the Fe(II) flow through measurements. Fe(II) leaches were conducted 2 weeks, 4 months and 9 months after the eruption. The trace metal leach experiments (above) were conducted at the same time as the first Fe(II) incubation experiments (2 weeks after ash collection).

~~In addition to dissolution experiments using Calbuco ash, for comparative purposes, suspensions of the following particles were also tested for Fe(II) release: volcanic ash retained from past eruptions (2002/Etna and 2008/Chaitén), dessert derived aerosols, glacial flour, iceberg borne particles and basalt/peridotite reference materials (see Supplementary Table).~~ For trace metal leaches, ~~Finally, for the analyses of the results,~~ the initial (mean ± standard deviation) dissolved trace metal concentrations were deducted from the final concentrations, in order to ~~appropriate~~ calculate the net change as a result of ash addition. For Fe(II) measurements, background levels of Fe(II) were below detection (<0.1 nM) and so no deduction was made.

2.3 Ash samples - Fresh and brackish water leaching experiments for total alkalinity, major ion and nutrient measurements

Fresh~~Both~~ brackish sub-surface water from the Patagonia study region (~~in Patagonia~~ was~~ere~~ obtained from the Aysén Fjord, at Ensenada Baja ~~,~~ (45º21’S: 72º40’W, salinity 16.3), close to the ~~because the laboratory for conducting this experiment was placed in~~ Coyhaique laboratory ~~-~~(Aysén region, Chile) and free from the influence of ash from the 2015 eruption~~, and considering the need for fresh fjord water, this place was chosen due to its vicinity from Coyhaique and because its~~ The oceanographic conditions in these waters ~~at the surface layer~~ are similar to the adjacent~~the ones from the~~ Reloncaví fjord (Cáceres et al., 2002; González et al., 2011). ~~and d~~De-ionized water, along with the Aysén fjord brackish water, were used for leaching experiments following ~~the~~ recommendations of Witham et al., (2005). Leaches were conducted in 50 ml LDPE bottles filled with either 40 ml brackish or ~~fresh~~ DI-water with 4 replicates of each treatment. Bottles were incubated inside a mixer at room temperature after the addition of 0.18 g ash, using two ash size fractions (<63 µm and 250-1000 µm) which were separated using sieves (ASTM e-11 specification, W.S. Tyler). The sampling times were at time zero (defined as just after the addition of the ash and a few minutes of mixing), 2 h and 24 h later. ~~Samples were immediately analyzed for total alkalinity (A_T) via a potentiometric titration.~~ Leaching experiments conducted with brackish water were analyzed for A_T via a potentiometric titration using reference standards (Haraldsson et al., 1997) ensuring a reproducibility of < 2 µmol/kg. For the de-ionized water leaching experiment, A_T was analyzed by titration of unfiltered 5 ml subsamples to a pH 4.5 endpoint (Bromocresol Green/Methyl Red) using a Dosimat (Metrohm Inc) and 0.02 N H_2SO_4 titrant. Alkalinity was calculated as $CaCO_3$ equivalents following APHA 2005-Methods 2320 (2320 Alkalinity, titration method). Additional 5 ml subsamples were filtered, stored at 4°C and analyzed within 3 days for major ions (Fl^-, Cl^-, SO_4^{2-}, NO_3^-, Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) ~~(Fl, Cl, SO_4, NO_3, Li, Na, NH_4, K, Mg, Ca)~~ using a DionexTM 5000 Ion Chromatography system with Eluent Generation (APHA). All measurements were then corrected for initial water concentrations prior to ash addition.

Table 1. Summary of different leaching experiments and samples. ~~DI water stand for de-ionized water.~~

Ash/ particle source	Experiment type-objective	Nº of replicates
~~Greenland, Iceberg embedded sediment~~	~~Trace metal leaching, seawater~~	~~3~~
~~Greenland glacial flour, sieved <63 µm~~	~~Trace metal leaching, seawater~~	~~3~~
~~Greenland glacial flour, sieved 63-106 µm~~	~~Trace metal leaching, seawater~~	~~3~~
~~Mali dessert sand, sieved <20 µm~~	~~Trace metal leaching, seawater~~	~~3~~
~~Saharan dessert dust collected in the Gibraltar Strait 1982~~	~~Trace metal leaching, seawater~~	~~3~~
~~Etna volcano ash, 2002 eruption~~	~~Trace metal leaching, seawater~~	~~3~~
~~Saharan dessert dust collected in Barbados 1967~~	~~Trace metal leaching, seawater~~	~~3~~
~~Reference material, basalt (USGS)~~	~~Trace metal leaching, seawater~~	~~3~~
~~Reference material, peridotite (USGS)~~	~~Trace metal leaching, seawater~~	~~3~~
~~Bodalsbreen glacial flour, Norway, sieved <63 µm~~	~~Trace metal leaching, seawater~~	~~3~~
~~Svalbard, Iceberg embedded sediment~~	~~Trace metal leaching, seawater~~	~~3~~
~~Chaitén volcano ash, Chilean Patagonia, 2008 eruption~~	~~Trace metal leaching, seawater~~	~~3~~
~~Calbuco volcano ash (0.5, 4 and 9 months aged respectively)~~	~~Trace metal leaching, seawater~~	~~3~~
Calbuco Volcano ash, sieved <63 µm	Total alkalinity, brackish water	4
Calbuco Volcano ash, sieved <63 µm	Total alkalinity, ion and nutrient leaching, DI water	4
Calbuco Volcano ash, sieved 250-1000 µm	Total alkalinity, brackish water	4
Calbuco Volcano ash, sieved 250-1000 µm	Total alkalinity, ion and nutrient leaching, DI water	4
Calbuco Volcanic ash, unsieved	Trace metal leaches, S Atlantic seawater	3
Calbuco Volcanic ash, unsieved	Fe(II) leaches, chilled S Atlantic	1*

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	seawater	

*1 time series of >10 measurements at 2-minute intervals following ash addition into seawater. DI, de-ionized water.

2.4 Environmental data – continuous Reloncaví Fjord monitoring

High temporal resolution (hourly) in situ measurements were taken simultaneously in the Reloncaví fjord (Fig. 1 C, North Patagonia Oceanographic Buoy) ~~at the sub-surface and~~ at the surface and at 3 m depth for *p*CO_2, pH, depth, temperature, conductivity and dissolved O_2 using two SAMI sensors that measured spectrophotometric CO_2 and pH (DeGrandpre et al., 1995; Seidel et al., 2008) (Sunburst Sensors, LLC), and an SBE 37 MicroCAT CTD-ODO (SeaBird Electronics) for temperature, conductivity, depth and dissolved O_2~~.~~, ~~Identical sets of instruments were deployed at the surface of Reloncaví Fjord and also at 3 m depth~~ as per Vergara-Jara et al., (2019). Sensor maintenance and quality control is described by Vergara-Jara et al., (2019). The error in *p*CO_2 concentrations is estimated to be at most 5% which arises mainly due to a non-linear sensor response and reduced sensitivity at high *p*CO_2 levels >1500 ppm (DeGrandpre et al., 1999). The SAMI-pH instruments used an accuracy test instead of a calibration procedure (Seidel et al., 2008). With the broad pH and salinity range found in the fjord, pH values are subject to a maximum error of ±0.02 (Mosley et al., 2004).

A meteorological station (HOBO-U30, Fig. 1) measured air temperature, solar radiation, wind speed and direction, rainfall, and barometric pressure every 5 minutes. Puelo River streamflow was obtained from the Carrera Basilio hydrological station (Fig. 1), run by Dirección General de Aguas de Chile (http://snia.dga.cl/BNAConsultas/reportes).

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2.5 Field surveys in Reloncaví Fjord post eruption

During May 2015, weekly field campaigns were undertaken in the Reloncaví Fjord. Phytoplankton samples were collected at 3 depths (1 m, 5 m and 10 m) for taxonomic characterization and abundance determination ~~(1 m, 5 m and 10 m)~~ at 3 stations (A, B and C; Fig. 1) using a 5 L Go-Flo bottle. Samples were analyzed using a Olympus CKX41 inverted phase contrast microscope using a 10 ml sedimentation chamber and the Utermöhl method (Utermöhl, 1958). The phytoplankton community composition was then statistically analyzed in R (RStudio V 1.2.5033) using general linear models in order to find statistically significant differences between dates and group abundances. Additionally, as part of a long-term monitoring program at station C (Fig. 1), on 6 occasions during March-May 2015, chlorophyll-a samples were retained from 6 depths (1, 3, 5, 7, 10 and 15 m). Chlorophyll-a was determined after filtering 250 ml ~~onto~~ of sampled water through GFF filters (Whatman) by fluorometry as per Welschmeyer (1994). Two additional profiles close to Station C were obtained from Yevenes et al., (2019). Integrated chlorophyll-a (mg m^{-2}) and diatom abundance (cells m^{-2}) ~~was~~ were determined to 15 m depth. Chlorophyll-a within Reloncaví Fjord is invariably concentrated in the upper ~10 ~~15~~ m (González et al., 2010; Yevenes et al., 2019) and thus, for comparison to prior data reported integrated to 10 m, only a small difference is anticipated. For all profiles considered herein (Fig. 4), there is a 20% difference between integrating to 10 m or 15 m depth ~~(González et al., 2010; Yevenes et al., 2019)~~. ~~Two additional profiles close to Station C were obtained from Yevenes et al., (2019).~~

2.6 Satellite data

Daily, 4 km resolution chlorophyll-a images from the MODIS Aqua sensor (OCI algorithm;

Hu et al., 2012) were downloaded from the NASA Ocean Color website (https://oceancolor.gsfc.nasa.gov) for the period 4 April 2015–2 May 2015. As a proxy for the spatial extent and loading of the ash plume, the UV aerosol index product from the Ozone Monitoring Instrument (OMI) on the EOS-Aura was downloaded for the same time period. Daily images were composited into 5-day mean averages (Fig. 7).

3. Results

3.1 In situ observations

The Calbuco ash plume reached up to 20 km height and was dispersed hundreds of kilometers across Patagonia and the Pacific and Atlantic Oceans (Fig. 2) (Eaton et al., 2016; Romero et al., 2016; Reckziegel et al., 2016). The ash loading in water bodies near the cone was visually observed to be high, especially near the Petrohué river catchment that drains into the head of the Reloncaví fjord. This ash loading into the fjord was clearly visible on 6 May 2015 when ash samples were collected for leaching experiments (Fig. 2).

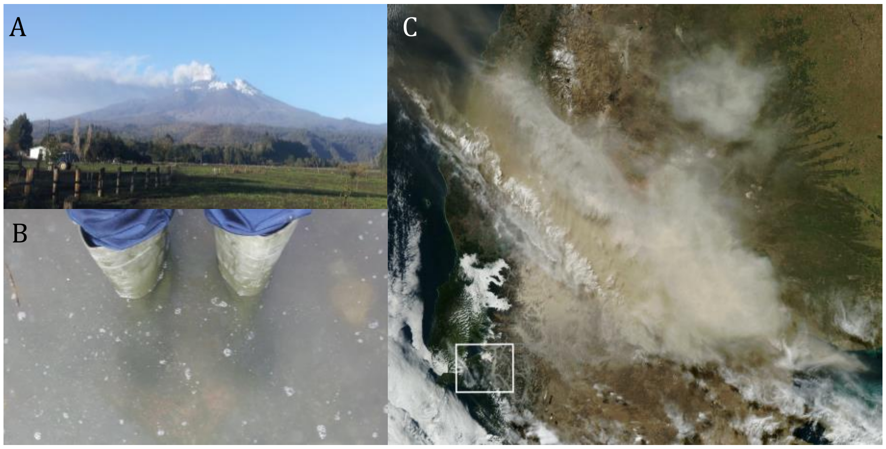

Figure 2. A Calbuco volcano ash plume May 6 2015. B Reloncaví Fjord water with atypical high turbidity due to the ash loading, Cochamó town 6 May 2015. C Ash cloud visible on MODIS Aqua satellite from the NASA Earth Observatory, April 23 (http://earthobservatory.nasa.gov/NaturalHazards/view.php?id=85767&eocn=home&eoci=nh). The highlighted box in C corresponds to Fig. 1 C.

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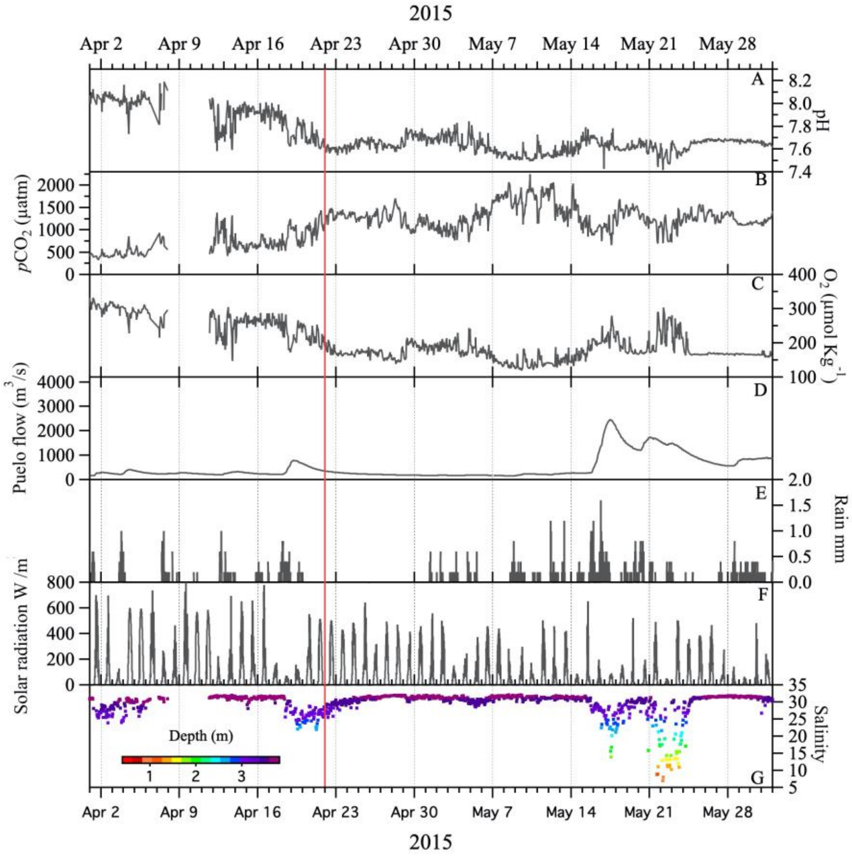

Figure 3 Continuous data from the Reloncaví Fjord mooring and nearby hydrological and weather stations for April-May 2015. The vertical red line marks the eruption date. All locations are marked in Fig 1. Carbonate chemistry and salinity data from Vergara-Jara et al., (2019). Wind and tidal mixing caused~~s~~ small changes in the depth of the ~~'surface'~~ sensors which are shown alongside the salinity data.

Carbonate chemistry data from the Reloncaví Fjord mooring demonstrated that pH declined and pCO_2 increased in the week prior to the eruption (22 April, Fig. 3). Oxygen and pH reached a minimum and pCO_2 a maximum during the time period May 7-14, which indicates a state of high respiration. In this stratified environment, the brackish fjord surface layer ha~~i~~s generally low pH, high pCO_2 with seasonal changes in salinity and respiration leading to a large annual range of pCO_2 and pH (Vergara-Jara et al., 2019). The depth of the sensors vari~~chang~~ed temporally due to changes in tides and river flow. This accounts for some of the variation in measured salinity due to the strong salinity gradient with depth in the brackish surface waters (Fig. 3). Any changes to pCO_2 or pH occurring as a direct result of the eruption, or associated ash deposition, are therefore challenging to distinguish from background variation due to~~as part of~~ short-term (intra-day) or seasonal shifts in the carbonate system which are pronounced in this dynamic and strongly freshwater influenced environment (Fig. 3). Freshwater discharge from the Puelo increased sharply from May 16 which is an annually recurring event (González et al., 2010).

3.2 Phytoplankton in Reloncaví fjord post-eruption

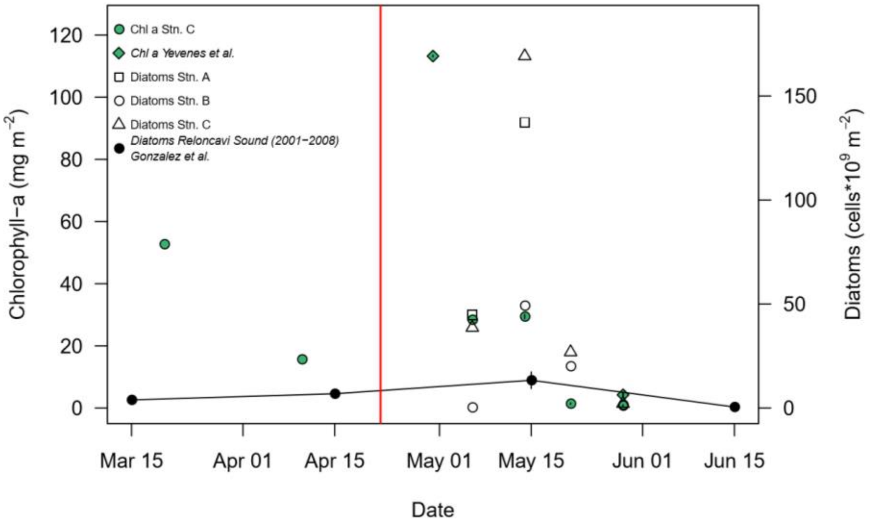

Figure 4. Changes in integrated (0-15 m) diatom abundance and chlorophyll-a for Reloncaví Fjord in April-May 2015. Locations as per Fig. 1, the eruption date (22 April) is marked with a red line. Historical diatom data from Reloncaví Sound (2001-2008, integrated to 10 m depth, mean ± standard error, González et al., 2010) and additional chlorophyll data from 2015 (‘Station 3’ from Yevenes et al., 2019, approximately corresponding to Station C herein) are also shown.

Phytoplankton abundances observed in May 2015 within Reloncaví Fjord were assessed by diatom cell counts and chlorophyll-a concentrations and were ~~comparable~~ proportionate to, or higher than, those previously observed~~measured~~ in the region (Fig. 4). When comparing observations to prior data~~Historical data~~ from González et al., (2010) ~~is not directly comparable with recent data~~ it should be noted that there is a slight depth discrepancy (earlier work was integrated to 10 m depth rather than 15 m herein). Yet as the phytoplankton bloom is overwhelmingly present within the upper 10 m these data do provide a useful comparison ~~but gives a site-seasonal useful context~~. Diatom abundance integrated to 15 m depth peaked at Stations ~~B~~ A and C ~~on~~ around ~~16~~ 14th May, with notably lower abundances at the more freshwater influenced station ~~A~~ B (Fig. 4), located at a mid-fjord site ~~that is at middle point~~ between the~~all~~ 3 major river outflows~~s~~. The h~~H~~ighest measured c~~C~~hlorophyll-a concentrations ~~at~~ were~~as~~ on 30th April at Station C, including two nearby measurements from Yevenes et al., (2019), ~~peaked on 30 April and~~then chlorophyll-a values declined to much lower concentrations in ~~June~~ late May which is expected from patterns in regional primary production (González et al., 2010). No measurements were available for 10-30 April 2015 (Fig. 4) and thus it is not possible to determine the timing of the onset of the austral autumn phytoplankton bloom with respect to the volcanic eruption from the available chlorophyll-a or diatom data. Within this time period, the mooring at Station C (Fig. 3) however did record a modest increase in pH and O_2 from 28-29 April, during a time period when river discharge and salinity were stable, which could be indicative of the autumn phytoplankton bloom onset.

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3.3 Total alkalinity and macronutrients in leach experiments

Size analysis of the collected ash determined a mean particle diameter of 339 µm. Small ash-particles (<63 µm) resulted in minor, or no significant, changes to A_T in brackish fjord waters (Fig. 5). With large ash-particles (>1.0 mm) no~~any~~ effect was~~ even less~~ evident. Conversely, a leaching experiment with de-ionized water showed a small increase in A_T (Fig. 5) for both size fractions. By increasing the A_T of freshwater, ash would~~ theoretically~~ act to increase the buffering capacity of river outflow into a typically weak carbonate system like the Reloncaví Fjord (Vergara-Jara et al., 2019). However, the absolute change in A_T was relatively small despite the large ash loading used in all incubations (< 20 µmol kg^{-1} A_T for ash loading >4 g

L^{-1}) and therefore it is expected that the direct effect of ash on A_T in situ was limited. Other effects on carbonate chemistry may however arise due to ash moderating the timing and intensity of primary production and thus biological pCO_2 drawdown.

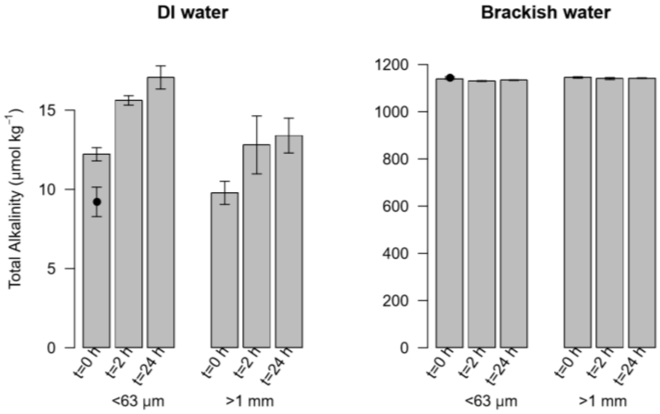

Figure 5. Total alkalinity released after leaching 4.5 g L^{-1} ash of two size fractions (<63 µm and >1.0 mm) in de-ionized water (DI water) and brackish water. T_0= 'time zero', measured after one minute of mixing, T_{2H}= after two hours of mixing, T_{24H}= after 24 hours of mixing. n=4 for all treatments (mean ± standard deviation plotted). The initial (pre-ash addition) alkalinity is marked by a black dot superimposed on the left T_0.

Ion c~~C~~hromatography results for Na, K, Ca, Fl, Cl, NO_3 and SO_4 showed that in the presence of smaller ash size particles, ion inputs were generally higher and that the ~~dissolution~~ leaching from ash components into de-ionized water occurred almost instantly with limited, or no increases in leached concentrations observed between 0, 2 and 24 h (Table 1). For larger particles there was less release of most ions. In the case of Ca and SO_4 a more gradual leaching effect was apparent (Table 2~~1~~). The concentrations of NO_3~~-~~ and~~,and~~ NH_4~~ and~~ were generally below detection suggesting that ash was a minor source of these ~~macro~~nutrients into solution. These observations are consistent with the trends in prior work using a range of volcanic ash and incubation conditions (Delmelle et al., 2007; Duggen et al., 2010; Witham et al., 2005).

	Time [h]	Na^+	K^+	Ca^{2+}	Fl^-	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+
Detection limit		*0.17*	*0.43*	*0.30*	*0.28*	*1.31*	*1.64*	*0.34*	*0.13*
Proced. Blank		b.d.	b.d.	0.39	b.d.	b.d.	b.d.	b.d.	b.d.
>1.0 mm [µmol/l]	0.1	3.4 (2.8)	0.83 (0.3)	18.3 (3.3)	0.16 (0.05)	3.7 (1.9)	3.7 (2.2)	b.d.	0.15 (0.2)
	2	5.1 (2.0)	1.0 (0.2)	18.5 (4.5)	0.21 (0.08)	4.4 (1.6)	4.9 (2.0)	b.d.	0.38 (0.4)
	24	7.3 (0.1)	1.4 (0.2)	23.4 (3.2)	0.52 (0.18)	5.7 (0.5)	8.3 (2.1)	b.d.	b.d.
<63 µm [µmol/l]	0.1	16.2 (12.7)	3.2 (0.3)	25.1 (5.4)	0.29 (0.0)	17.1 (13.6)	13.5 (1.3)	0.53 (0.2)	1.70 (1.1)
	2	16.7 (1.0)	3.8 (0.1)	31.8 (2.7)	0.63 (0.2)	15.2 (0.9)	19.0 (0.3)	b.d.	0.52 (1.0)
	24	17.3 (0.8)	3.9 (0.3)	33.8 (3.3)	0.69 (0.3)	14.6 (1.0)	18.8 (0.5)	b.d.	1.32 (2.6)
<63 µm [µmol/g ash]	24	3.84	0.87	7.50	0.15	3.25	4.18	0.048	0.29
	Range (lit.)	1.5-84.3	0.1-5.4	0.6-589	0.1-9	2-92.9	1-554	0-6.4	0.3-0.6

Table 2. Major ion and macronutrient concentrations in µmol/l leached from the two size fractions of ash (< 63 µm and >1.0 mm) into deionized water (b.d. = below detection). Shown are mean, with standard deviation in parentheses (n=4). Also shown are mass normalized values [µmol/g ash], and a comparison to the range of values reported by Jones and Gislason, (2008)

3.4 Trace elements in leach experiments

Release of nanomolar concentrations of dissolved Fe and~~,~~ Mn ~~and Cu~~ was evident when ash was re-suspended in aged seawater for 10 minutes (Fig. 6). ~~The efficiency of dFe release from volcanic ash was variable with the most efficient release of dFe per unit mass of ash addition (1200 nmol g^{-1}) achieved at the lowest loading per unit volume of seawater tested (<10 mg L^{-1}) (Fig.7 right)~~. ~~Conversely,~~ T~~t~~he net release of dissolved metals proceeded with varying relationships with ash loading over the~~ Mn and Cu increased linearly (R^2 0.99) over the~~ applied~~ ash~~ gradient (0.1 - 6 mg L^{-1}). Dissolved Mn, Pb, Cu and Co release exhibited significant ($p < 0.05$) positive relationships with ash loading, with Mn and Cu exhibiting the most linear behavior (R^2 0.99 and 0.83, respectively).~~.~~ ~~This demonstrates that the reduced dissolution efficiency of Fe at high particle loads was related to the chemistry of dFe which is a readily scavenged element in seawater (de Baar and de Jong, 2001; Johnson et al., 1997).~~ ~~Dissolved~~

~~Mn and Cu concentrations increased with ash loading similarly Co, Pb and Ni have apparent increase but with weaker linear relationships between metal concentration and ash loading and overlaping error bars (Fig. 6)~~~~Dissolved Co, Pb and Ni concentrations increased with ash loading similarly to Mn and Cu, but with weaker linear relationships between metal concentration and ash loading (Fig. 6). No clear increase in dissolved Cd concentrations was evident with increased ash loading.~~ ~~Non-linearity between ash addition and trace metal concentrations, and negative changes in concentrations under some conditions, both likely reflect scavenging of metal ions onto ash particle surfaces (Rogan et al., 2016).~~The initial concentration of metals in South Atlantic seawater should however also be considered when interpreting the trends. The magnitude of changes in Cd and Ni concentrations were smallest relative to both the initial concentration and the standard deviation on the initial concentration (0.38 ± 0.04 nM Cd and 6.58 ± 0.76 nM Ni, respectively). It thus would be difficult to extract a clear relationship irrespective of their chemical behavior. For other elements, n~~N~~on-linearity between ash addition and trace metal concentrations, and some negative changes in concentrations~~ under some conditions~~, both likely reflect scavenging of metal ions onto ash particle surfaces (Rogan et al., 2016). Fe, Co and Pb are all scavenged type elements and so increasing the surface area of ash present may affect the net change in metal concentration.

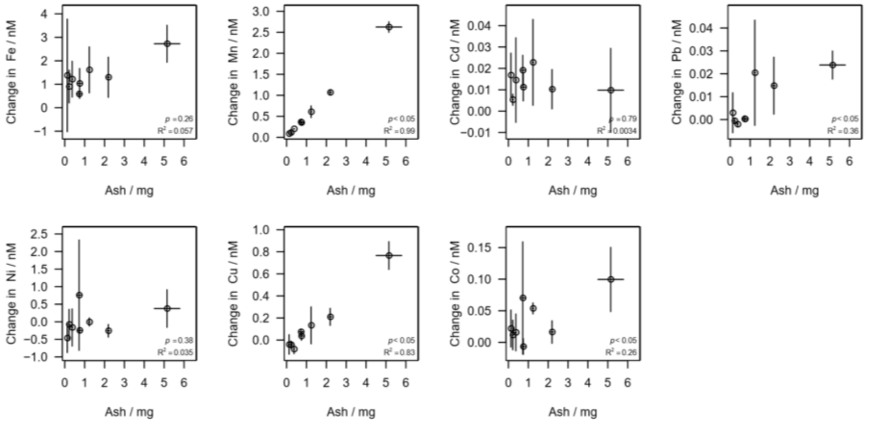

Figure 6. Change in trace metal concentrations after varying ash addition to 100 ml South Atlantic seawater for a ~~10 minute~~10-minute leach duration at room temperature. Initial (mean ± standard deviation) dissolved trace metal concentrations - deducted from the final concentrations to calculate the change as a result of ash addition - were 0.98 ± 0.03 nM Fe, 0.38 ± 0.04 nM Cd, 13 ± 2 pM Pb, 6.58 ± 0.76 nM Ni, 0.84 ± 0.07 nM Cu, 145 ± 9 pM Co, 0.72 ± 0.05 nM Mn. Error bars are standard deviations from triplicate treatments with similar ash loadings. p~~P~~ values and R^2 for a linear regression are annotated~~ and refer to the total dataset rather than the mean of each triplicate~~.

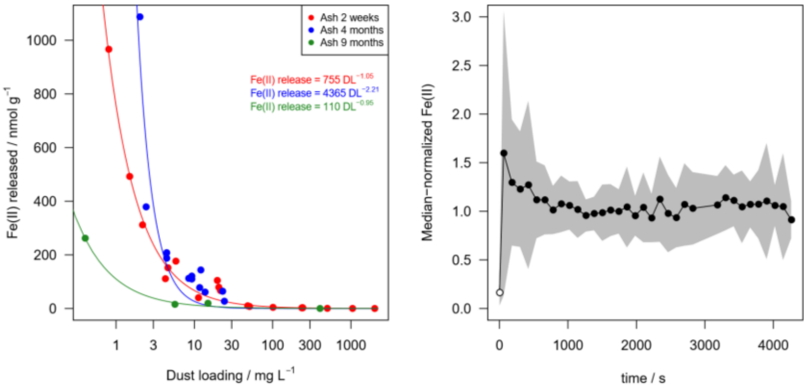

Figure 7. Fe(II) release from ash into seawater. Mean Fe(II) released into South Atlantic seawater over a 30 minute leach at 5-7°C (left). The same batch of Calbuco ash was subsampled and used to conduct experiments on 3 occasions after the 2015 eruption (2 weeks, 4 months and 9 months since ash collection).~~ and contrasted with other aged particles from different sources including volcanic ash retained from the 2002/2008 eruptions of Etna and Chaitén respectively (see Supplementary Table). Dissolved Fe released into South Atlantic seawater over a 10 minute leach at room temperature, data as per Fig. 6 with individual replicates shown for clarity (right).~~ The 30 minute time-series of Fe(II) concentrations following ash addition are considered collectively by normalizing the measured concentrations (right), such that 1.0 represents the median Fe(II) concentration measured in each experiment 2-30 minutes after ash addition. The black line shows the mean response over 34 leach experiments with varying ash loading, the shaded area shows ± 1 standard deviation. The initial Fe(II) concentration (pre-ash addition at 0 s) in all cases was below detection and thus the detection limit is plotted at 0 s (open circle).

In addition to the release of dFe in solution, which generally exists as Fe(III) species in oxic seawater (Gledhill and Buck, 2012), the release of Fe(II) was evident on a similar timescale when cold (5-7°C) aged S Atlantic seawater was used as leachate (Fig. 7). The half-life of Fe(II) decreases more than tenfold as temperature is increased from 5 to 25°C, leading to Fe(II) decay on timescales shorter than the time required for analysis (approximately 60 s for solution to enter the flow injection apparatus, mix with reagent and generate a peak) (Santana-Casiano et al., 2005). Elevated concentrations of up to 4.0 nM Fe(II) were evident at this temperature (5-7°C), which represents an intermediate sea surface temperature for the high latitude ocean~~ when ash was suspended in cold (5-7°C) aged S Atlantic seawater (Fig.~~

~~6)~~. A sharp decline in Fe(II) dissolution efficiency with increasing ash load was also evident (Fig. 7). Both the highest Fe(II) concentration~~,~~ and the highest net release of Fe(II)~~,~~ were~~as~~ observed at the lowest ash loading (Fig. 7). ~~Fe(II) release was more intense for freshly collected ash particles at low ash loadings, but traces of Fe(II) were found to be released from similar suspensions of other particle types (Saharan dust, glacial flour, iceberg borne particles) at intermediate loadings and from two other aged volcanic ash samples stored since 2002/2008 (Fig. 7).~~

~~For Calbuco volcanic ash,~~ Fe(II) concentration following dust addition into seawater was possibly~~noticeably~~ reduced when the same experimental leaches with ash were repeated 9 months after the initial experiment. The first leaches were conducted ~2 weeks after ash collection. The ~~release of Fe(II) from ash therefore appeared to decrease with aging after several month~~absence of a clear change between 2 weeks and 4 months precludes an accurate assessment of the rate at which Fe(II) solubility may have decreased.

As Fe(II) concentrations were measured continuously using flow injection analysis, the temporal development of Fe(II) concentration after ash addition to cold seawater can also be shown (Fig. 7). Considering the set of leach experiments collectively, all ash additions were characterized by a sharp increase in Fe(II) concentrations in the first minute after ash addition into seawater. This was typically followed by a decline and then a relatively stable Fe(II) concentration. ~~For comparison, the trace metal leach experiments (Fig. 6) were conducted at the same time as the first Fe(II) incubation experiments (i.e. 2 weeks after ash collection).~~

3.5 Satellite observations

Five-day composite images of atmospheric aerosol loading (UV aerosol index) indicated two main volcanic eruption plume trajectories: (i) northwards over the Pacific, and (ii) northeast over the Atlantic. Daily resolved time series were constructed for regions in the Atlantic and Pacific with elevated atmospheric aerosol loading (UV Aerosol Index ~2 a.u.; Fig. 8). The Pacific time series indicated a pronounced peak in aerosol index followed by chlorophyll-a one day later. 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.

Conversely in the Atlantic, where the background chlorophyll-a concentration was higher throughout the time period of interest, the main area with enhanced aerosol index was not clearly associated with a change in chlorophyll-a dynamics on a timescale comparable to that observed following other volcanic ash fertilized events (Fig. 8). In a smaller ash impacted area to the south of the Rio de la Plata (Supplementary Fig.), where nitrate levels are expected to be higher than to the north and Fe levels also expected to be elevated due its location on the continental shelf, a chlorophyll-a peak was evident 7 days after the UV aerosol peak. However, this was not well constrained due to poor satellite coverage in the period after the eruption.

Prior eruptions have been attributed with driving time periods of enhanced regional marine primary production beginning 3-5 days post-eruption (Hamme et al., 2010; Langmann et al., 2010; Lin et al., 2011) and bottle experiments showing positive chlorophyll changes in response to ash addition are typically significant compared to controls within 1-4 days following ash addition (Browning et al., 2014b; Duggen et al., 2007; Mélançon et al., 2014).

Figure 8. Potential biological impact of the 2015 Calbuco eruption observed via satellite remote sensing. (A-F) Spatial maps showing the distribution of ash in the atmosphere (UV Aerosol Index) and corresponding images of chlorophyll-a. Images were composited over 5-

day periods. Grey lines in chlorophyll maps corresponds to the UV Aerosol index = 2 a.u. contour. (G, H) Time series of UV Aerosol Index and chlorophyll-a for regions of the Pacific (G) and Atlantic (H) identified by boxes in maps. Dashed vertical lines (22 April) indicate the eruption date. (I) Mean World Ocean Atlas surface NO_3 concentrations. Thin black lines indicate the 500 m bathymetric depth contour.

4 Discussion

4.1 Local drivers of 2015 bloom dynamics in Reloncaví Fjord

The north Patagonian archipelago and fjord region have a seasonal phytoplankton bloom cycle with peaks in productivity occurring in May and October (austral autumn and spring) and the lowest productivity consistently in June (austral winter) (González et al., 2010). Diatoms normally dominate the phytoplankton community during the productive period due to high light availability and high silicic acid supply, both of which are influenced by freshwater runoff (González et al., 2010; Torres et al., 2014). The austral fall season, encompassing the April-May 2015 ash fall, is therefore expected to have a high phytoplankton biomass (Iriarte et al., 2007; León-Muñoz et al., 2018) which terminates abruptly with decreasing light availability in austral winter (González et al., 2010).

Whilst not directly comparable, the magnitude of the 2015 bloom in terms of diatom abundance (Fig. 4) was more intense than that reported in Reloncaví Sound 2001-2008. With respect to the timing of the phytoplankton bloom, the low diatom abundances and chlorophyll-a concentrations at the end of May (Fig. 4) are consistent with prior observations of sharp declines in primary production moving into June (González et al., 2010). Peaks in diatom abundance were measured at two stations on 14th~~6~~ May, and measured chlorophyll-a concentrations were highest close to Station C on 30 April (Fig. 4). Station A, with the strongest freshwater influence, did not show such a pronounced peak in diatom abundance (Fig. 3). The high-resolution pH and O_2 data collected at Station C from mooring data is consistent with an intense phytoplankton bloom between ~29 April and 7 May (Fig. 3) indicated by a shift to slightly higher pH and O_2 during this time period when river flow into the fjord was stable.

Without a direct measure of ash deposition per unit area ~~m^{-2}~~ in the fjord, turbidity, or higher resolution chlorophyll/diatom data, it is challenging to unambiguously determine the extent to which the austral autumn phytoplankton bloom was affected by volcanic activity. The high abundance of diatoms at two of three stations sampled could have resulted from ash fertilization. Yet if this was the case, it is not clear which~~questionable what~~ nutrient was responsible for this fertilization, why the bloom initiation occurred several weeks after the eruption, and to what extent the timing was coincidental given that productivity normally peaks in May. Reloncaví Fjord was to the south of the dominant ash deposition (Romero et al., 2016). Both runoff and rainfall were vectors by which ash was deposited in the fjord, which complicates the interpretation of the time series provided by high resolution data (Fig. 3). With incident light also highly variable over the time series (Fig. 3F), there are clearly several factors, other than volcanic ash deposition, which will have exerted some influence on diatom and chlorophyll-a abundance throughout May 2015.

Primary production in the Reloncaví region is thought to be limited by light availability rather than macronutrient availability (González et al., 2010). Whilst micronutrient availability relative to phytoplankton demand has not been extensively assessed in this fjord, with such higher riverine inputs across the region- which are normally a large source of dissolved trace elements into coastal waters (e.g. Boyle et al., 1977)- limitation of phytoplankton growth by Fe, or another micronutrient, seems implausible. Reported Fe concentrations determined by a diffusive gel technique in Reloncaví Fjord in October 2006 were ~~found to be~~ relatively high; 46-530 nM (Ahumada et al., 2011). Similarly, reported dFe concentrations in the adjacent Comau Fjord at higher salinity are generally in the nanomolar range and remain >2 nM even under post-bloom conditions which suggests dFe is not a limiting factor for phytoplankton growth (Hopwood et al., 2020; Sanchez et al., 2019).

Silicic acid availability could have been increased by ash deposition. Whilst not quantified herein, an increase in silicic acid availability from ash in a region where silicic acid was sub-optimal for diatom growth could ~~therefore~~ plausibly explain higher than usual diatom abundance (Siringan et al., 2018). Silicic acid concentrations were indeed high (up to 80 µM) in Reloncaví Fjord surface waters in May 2015 (Yevenes et al., 2019), however concentrations in excess of 30 µM are typical during periods of high runoff and accordingly are not thought to limit primary production or diatom growth (González et al., 2010). The Si:NO_3 ratio in Reloncaví Fjord and downstream Reloncaví Sound also indicates an excess of Si, with ratios of approximately 2:1 observed in fjord surface waters throughout the year (González et al., 2010; Yevenes et al., 2019). For comparison, the ratio of Si:N for diatom nutrient uptake is 15:16 (Brzezinski, 1985). Furthermore, experimental incubations making additions of macronutrients to fjord waters in Reloncaví and adjacent fjords, have found strong responses of phytoplankton to additions of Si only when Si and NO_3 were added in combination, further corroborating the hypothesis that an excess of Si is normally present in surface waters of these fjord systems (Labbé-Ibáñez et al., 2015). It is therefore doubtful that changes in nutrient availability from ash alone could explain such high diatom abundances in mid-May.

Alternative reasons for high diatom abundances in the absence of a chemical fertilization effect are plausible and could include, for example, ash having reduced zooplankton abundance or virus activity in the fjord, thus facilitating higher diatom abundance than would otherwise have been observed by decreasing diatom mortality rates in an environment where nutrients were replete. The role of volcanic ash in driving such short-term ecological shifts in the marine environment is almost entirely unstudied (Weinbauer et al., 2017). However, volcanic ash deposition of ~~+~~7 mg L^{-1} in lakes within this region during the 2011 Puyehue-Cordón Caulle eruption was reported to increase post-deposition phytoplankton biomass and decrease copepod and cladoceran biomass (Wolinski et al., 2013). The proposed mechanism was ash particle ingestion negatively affecting zooplankton and ash-shading positively affecting phytoplankton via reduced photoinhibition (Balseiro et al., 2014; Wolinski et al., 2013).

Considering the more modest peak in diatom abundance at the most strongly ash affected station (Station A, Fig. 4) and the timing of the peak diatom abundance 3 weeks after the eruption, it is clear that the interaction between ash and phytoplankton in the Reloncaví Fjord was more complex than the simple Fe-fertilization proposed for the SE Pacific (Fig. 8g). In the absence of an immediate diatom fertilization effect from Fe or silicic acid, we hypothesize that any change in phytoplankton bloom dynamics within Reloncaví Fjord was mainly a ‘top-down’ effect driven by the physical interaction of ash and different ecological groups in a nutrient replete environment, rather than a 'bottom-up' effect driven by alleviation of nutrient-limitation from ash dissolution.

4.2 Volcanic ash as a unique source of trace elements

The release of the bioessential elements Fe and Mn from ash here ranged from 53 - 1200 nmol g^{-1} (dFe) and 48 - 71 nmol g^{-1} (dissolved Mn), which is comparable to the rates determined in other studies under similar experimental conditions (Duggen et al., 2010)~~, although the dFe released at the lowest ash loading is at the high end of reported values (Fig. 76)~~. A contrasting relationship was observed between the release of dFe and Fe(II) as ash loading was changed. ~~Neither Fe(II) or dFe release increased linearly with ash loading, with the~~ Fe(II) release was particularly efficient at ash loadings <5 mg L^{-1} (Fig. 7) whereas dFe release was less sensitive to ash loading (Fig. 6).

The timing of Fe(II) release in the first 60 s of incubations suggests a fast dissolution process. ~~Unlike dissolved Cu and Mn, a more efficient release of dFe at low ash loading highlights the dual role of ash particles as both a source of dFe and also a large surface area onto which metal ions can be scavenged (Rogan et al., 2016).~~

Fe(II) is short lived in oxic surface seawater with an observed half-life of only 10-20 minutes even in the~~ cold surface waters of the~~ Southern Ocean where cold surface waters~~ich~~ slow Fe(II) oxidation (Sarthou et al., 2011). Yet, relative to Fe(III), Fe(II) is also more soluble and, from an energetic perspective, expected to be more bioaccessible to cellular uptake (Sunda et al., 2001). ~~Fe(II) salts are expected to be present on the surface of ash particles (Horwell et al., 2003; Hoshyaripour et al., 2015) and thus Fe(II) may be released into seawater almost instantaneously when fresh deposition of volcanic ash occurs following dissolution of thin layers of salt coatings in ash surfaces (Ayris and Delmelle, 2012; Delmelle et al., 2007).~~

Whilst it is known that the vast majority of dFe leached from ash into seawater tends to occur in the first minutes of ash addition (Duggen et al., 2007; Jones and Gislason, 2008) and this could be consistent with rapid dissolution of highly soluble phases on ash surfaces, we note that there is not yet conclusive evidence concerning the precise origin of this Fe pulse. Fe(II) salts may be present on the surface of ash particles (Horwell et al., 2003; Hoshyaripour et al., 2015) and thus the Fe(II) observed herein (Fig. 7) may reflect almost instantaneous release following dissolution of thin layers of salt coatings in ash surfaces (Ayris and Delmelle, 2012; Delmelle et al., 2007; Olsson et al., 2013). Alternatively Fe(II) could be released from more crystalline Fe(II) phases.

~~Upon aging of dry ash, the Fe(II) concentration leached from ash decreased sharply between 4 and 9 months after the eruption, suggesting an on-going conversion of Fe(II) to Fe(III) on ash particle surfaces (Fig. 7). The precise cause of this is uncertain from our experiments, yet we can speculate that as Fe(II) on fresh ash surfaces is expected to be associated with acidic surface coatings, it could be a 'self-neutralization' effect where the low surface pH of Fe(II)-rich zones is slowly neutralized by interaction with the more alkaline bulk material. Irrespective of the underlying cause, this implies that the bioavailability of Fe within freshly deposited ash would be higher than aged ash, or other un-processed aerosols. Standard leaching protocols are thereby unlikely to resolve the release of Fe(II) that could occur under environmentally relevant conditions.~~ Different leaching protocols are widely recognised as a major challenge for interpreting and comparing different dissolution experiment datasets for all types of aerosols (Duggen et al., 2010; Morton et al., 2013). When Fe(II) is released into solution as a considerable fraction of the total dFe release this is particularly challenging, as Fe(II) oxidises on timescales of seconds to minutes depending on temperature, pH and O_2 conditions (Santana-Casiano et al., 2005). ~~In any case, a decline in the release of dFe from~~

~~volcanic ash upon aging under the same storage conditions (bulk dry samples) has been noted previously (Duggen et al., 2010), but was thought to be a slow process with a time period of 10-20 years required for the dFe leached within an hour in seawater to fall by half (Olgun et al., 2011). The much more rapid 50-90% decline in the Fe(II) released into seawater occurring between 2 weeks and 9 months after the eruption likely reflects much faster changes in the surface composition of ash which may not be evident in leaches conducted under conditions unfavourable for Fe(II) release (e.g. at room temperature), or when baseline experimental leaches for evaluating aging effects are conducted several months after the collection of ash.~~

The dFe and Fe(II) leaching protocols used herein are only~~not directly~~ comparable qualitatively, as the Fe(II) method using cooler seawater and larger seawater volumes was specifically designed to test for the presence of rapid Fe(II) release and to evaluate the short-term temporal trend of any such release. Yet, for rough comparative purposes, the Fe(II) released was equivalent to 38 ± 25% (mean ± standard deviation) of dFe released at ash loadings from 1-10 mg L^{-1} and 19 ± 17% of dFe for ash loadings from 10-50 mg L^{-1}. These values are reasonably comparable to the 26% median Fe(II)/dFe fraction measured in Fe released into seawater from aerosols collected over the Pacific Ocean (Buck et al., 2013) suggesting that fresh volcanic ash is roughly comparable in terms of Fe(II) lability to these environmentally processed aerosols.

4.3 A potential fertilization effect in the SE Pacific

Experiments with ash suspensions have shown that ash loading has a restricted impact on satellite chlorophyll-a retrieval (Browning et al., 2015), 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).~~, 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. Also, 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 iron levels also expected to be elevated due its location on the continental shelf, also 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..~~ Following the eruption date, mean chlorophyll-a concentrations increased ~2.5 times over a broad region where elevated UV aerosol index~~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 (Hamme et al., 2010) which was similarly thought to be triggered by relief of Fe-limitation (Langmann et al., 2010). 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 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.

The change in chlorophyll-a observed in the SE Pacific contrasts with results in Reloncaví Fjord where phytoplankton abundances were lowest at the strongest ash-influenced station (Station A, Fig.1) and likely peaked much later than the first ash arrival- after 28 April. The fertilized region of the Pacific (Fig. 8) hosts upwelling of deep waters, supplying nutrients in ratios that are deficient in dFe (Bonnet et al., 2008; Torres and Ampuero, 2009). Fe-limitation of phytoplankton growth in this region is therefore anticipated, which could have been temporarily relieved following ash deposition and dFe release (Fig. 6). 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 proceeded 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).~~Conversely, ash deposition into the south western Atlantic indicated by atmospheric aerosol loading did not lead to any clear corresponding change in chlorophyll-a concentrations (Fig. 8H).~~ Phytoplankton growth in this region of the Atlantic is expected to be limited by fixed nitrogen availability, as a result of strong stratification (Moore et al., 2013) and thus dFe release from ash particles would not be expected to result in short-term increases to primary production. The differential responses observed in the Pacific and Atlantic are therefore consistent with the anticipated nutrient limitation regimes (Fe-limited and nitrogen-limited, respectively), and the supply of dFe but not fixed N (NO_3 or NH_4) from the Calbuco ash (Fig. 6 and Table 1).

5 Conclusions

The contrasting effects of volcanic ash on primary producers in Reloncaví Fjord, ~~the~~ SE Pacific and SW Atlantic support the hypothesis that the response of primary producers is ~~highly~~ dependent on both the ash loading and the resources limiting primary production in a region at a specific time of year. Leach experiments using ash from the 2015 Calbuco eruption demonstrated a small increase in the alkalinity of de-ionized water from fine, but not coarse ash, and no significant addition of fixed nitrogen (quantified as NO_3 and NH_4) into solution. In saline waters, release of dissolved trace metals including Mn, Cu, ~~Ni,~~ Co, Pb, Fe and specifically Fe(II) was evident.

Strong evidence of a broad-scale 'bottom-up' fertilization effect of ash on primary production was not found locally within Reloncaví Fjord, although it is possible that the timing and peak diatom abundance of the autumn phytoplankton bloom may have shifted in response to high ash loading in the weeks following the eruption. High diatom abundances at some stations within the fjord several weeks after the eruption may have arisen from a 'top-down' effect of ash on filter feeders, although the mechanism can only be speculated herein. No clear positive effect of ash deposition on chlorophyll-a was evident in the SW Atlantic, consistent with expected patterns in nutrient deficiency which suggest the region to be nitrogen-limited. However, in offshore waters of the SE Pacific where Fe is anticipated to limit phytoplankton growth, chlorophyll-a ~~a~~increase was related with ~~close correlation between~~ maximum ash deposition and ~~an~~ we presume that that increase in chlorophyll-a was likely driven by Fe-fertilization.

6. Data availability

The complete 2015 time series from the Reloncaví Fjord mooring is available online (https://figshare.com/articles/Puelo_Bouy/7754258). Source data for Figures 4-7 is included in the Supplement.

7. Acknowledgements

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9. Author contributions

MVJ, MH, JLI and EA designed the study. MVJ, IR, MH, RT and BR conducted analytical and field work. TB conducted satellite data analysis. MV, MH and TB wrote the initial manuscript with all authors contributing to its revision.

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