A mosaic of phytoplankton responses across Patagonia, the southeast Pacific and southwest Atlantic Oceans to ash deposition and trace metal release from the Calbuco 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 eruption of the Calbuco volcano in April 2015, an extensive ash plume spread across northern Patagonia and into the southeast Pacific and southwest Atlantic Oceans. Here we report on field surveys conducted in the coastal 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~~F$^-$, Cl$^-$, SO_4^{2-}, NO_3^-, Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). Within Reloncaví Fjord, integrated peak diatom abundances during the May 2015 austral bloom were approximately 2-4 times 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 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 Atlantic where the availability of fixed

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nitrogen is thought to limit phytoplankton growth. This was consistent with no significant release of fixed nitrogen (NO_x or NH_4) from ~~the~~Calbuco 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 ash were an unusually prolific source of Fe(II) into chilled seawater (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. A pulse of Fe(II) release upon addition of Calbuco ash to seawater made it an unusually efficient dissolved Fe source ~~with the ~18-38%~~. The fraction of dissolved Fe released as Fe(II) from Calbuco ash (~18-38%) was 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.~~following long range atmospheric transport.

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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-micronutrient 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 (Hoffmann et al., 2012; Newcomb and Flagg, 1983; Stewart et al., 2006). Surveys directly underneath the ash plume from the 2010 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 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., 2014; Hoffmann et al., 2012), into seawater. In contrast, apart from inducing light limitation, there are several adverse effects of ash deposition on aquatic organisms. These include metal toxicity (Ermolin et al., 2018), particularly under high dust loading (Hoffmann et al., 2012), and 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

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in some, but not all, ash leaching experiments and in some ~~fresh waterbodies~~freshwater bodies following intense ash falls, suggesting that significant ash deposition on weakly buffered aquatic environments can also impact and perturb their carbonate system (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 macronutrients or light, rather than trace elements, limit primary production.

In contrast to the ~~North Atlantic 2013~~2010 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 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 carried out on ash collected from the fjord region, to investigate the inorganic consequences of ash addition to ~~solution~~natural waters. We thereby evaluate the potential positive and negative effects of ash from the 2015 Calbuco eruption on

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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~~in close proximity to 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, and Cochamó, with mean stream flows of 650 $m^3 s^{-1}$, 350 $m^3 s^{-1}$ and 100 $m^3 s^{-1}$, 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)~~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 (>1 g C m^{-2} day^{-1}) throughout austral spring, summer and early autumn (González et al., 2010).

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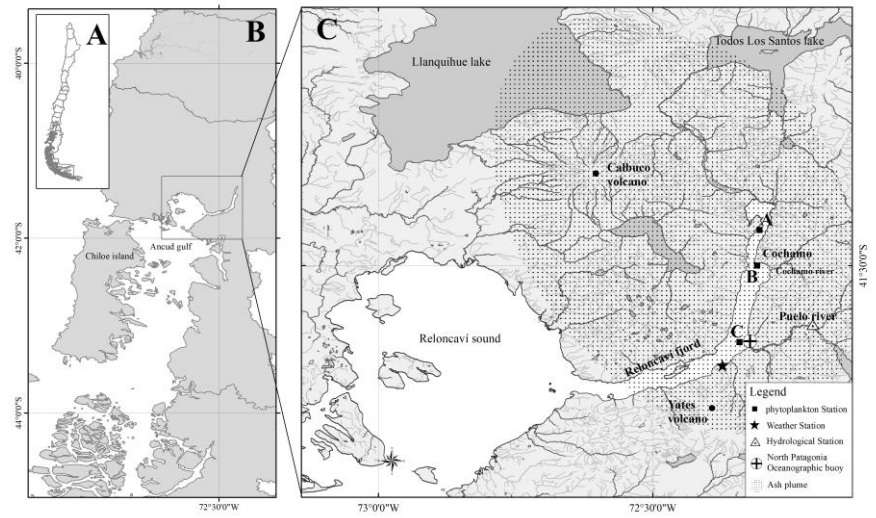

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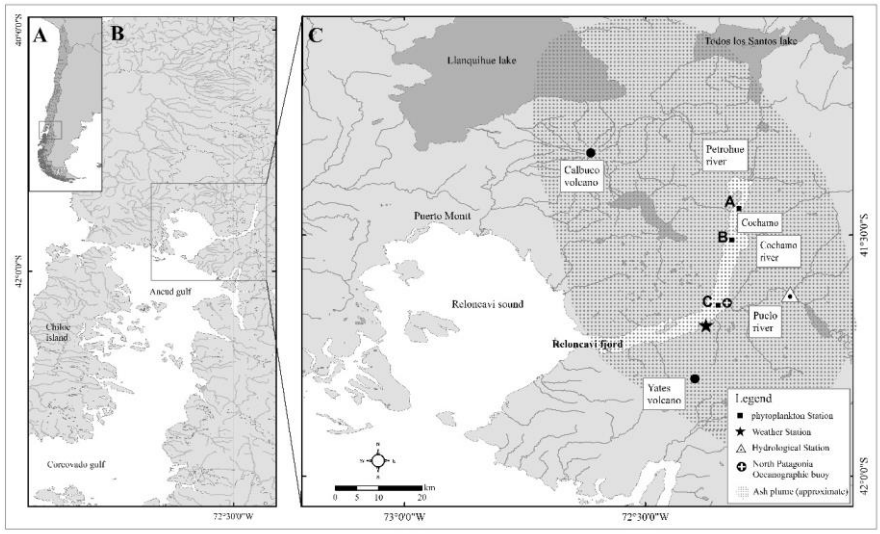

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Figure 1. The Calbuco region showing the location of Reloncaví Fjord, 3 major rivers (Petrohué, Cochamó and Puelo) discharging into the fjord, the 3 stations (black squares; A, B and C) used to assess changes in phytoplankton abundance following the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

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). A smaller eruption occurred on 30 April projecting ash 4-5 km above sea level which was then mainly deposited south of the volcano. Smaller volumes of ash were released semi-continuously for three weeks after the main eruption, leading to intermittent ash deposition events. 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~~complement 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 daily technical reports including the estimated area of

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ash dispersion (http://sitiohistorico.sernageomin.cl/volcan.php?pagina=4&iId=3). This information was used to create a reference aerial extent of ash deposition for the week after the eruption (Fig. ~~1, C).~~1, C) and this approximation represents a full week of coverage for this dynamic feature.

2.2. Ash samples – trace metal leaching experiments

~~Ash (500 g) was collected (~~On 6 May (2015, ~~in~~ Cochamó, Chile~~),~~, approximately 30 km from the volcano) after the third, and smallest, eruptive pulse of ash from the Calbuco volcano (Fig. 2, A), and with the volcano still emitting material, ash was collected using a plastic tray wrapped with plastic sheeting (40 × 94 cm~~),~~). The plasticware was left outside for 24 hours until sufficient ash (~500 g) was collected to provide a bulk sample. Ambient weather over the period of ash collection, and the preceding day, was dry (no precipitation). The collected ash was 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~~

Ash may affect in situ phytoplankton dynamics in several ways, for example via moderating the carbonate system, macronutrient availability and/or micronutrient availability. As micronutrient (e.g. Fe and Mn) availability is expected to be the main chemical mechanism via which phytoplankton dynamics in the offshore marine environment could be affected, we primarily focus our investigation on the release of dissolved trace metals from ash in seawater ~~for~~. Yet to rule out other potential affects, we also conduct complementary leaches to assess the significance of changes to total alkalinity and macronutrient availability (Table 1). For

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trace metal leaches, a variety of methods have been used in the literature (Duggen et al., 2010; Witham et al., 2005) depending on the purpose of specific studies. De-ionized water leaches with ash loadings that are high in an offshore environmental context are preferable for intercomparison studies. The trace metals released under such conditions are however difficult to compare quantitatively to metal exchange processes in the ambient marine environment, especially for elements such as Fe where solubility is strongly influenced by pH, salinity and the nature of dissolved organic carbon present (Baker and Croot, 2010). For prior work conducted specifically using volcanic ash in seawater, 3 main methods have been employed: suspension experiments followed by analysis of the leachate, flow-through reactors, and continuous voltammetric determination of dFe concentrations in situ during suspension experiments (Sup. Table 1). The most commonly used ash:solute ratio in prior seawater experiments is 1:400 (g:mL), with leach lengths varying from 15 minutes to 24 hours (Sup. Table 1). Conversely, incubation experiments ~~was collected in the~~ designed to test the response of marine phytoplankton to ash deposition have used lower ash:solute ratios of 1:400 to 1:10^7 which are based on estimates of the ash loading expected to be mixed within the offshore surface mixed layer underneath ash plumes (Browning et al., 2014; Hoffmann et al., 2012). Existing data suggests that ash:solute ratio is not a major factor in determining the release behavior of Fe from ash, however this is acknowledged to be difficult to assess due to other differences between experimental setups used to date (Duggen et al., 2010). Both the age of particles since collection and the organic carbon content of seawater are however known to be critical factors influencing the exchange of Fe, and other trace elements, following any aerosol deposition into seawater (Baker and Croot, 2010; Duggen et al., 2010). Whilst UV-treatment of seawater has been used in some experiments (to remove

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a large part of any natural organic ligands present, Duggen et al., 2007; Jones and Gislason, 2008), and a strong synthetic organic ligand added in others (to impede dissolved Fe precipitation, Duggen et al., 2007; Olgun et al., 2011; Simonella et al., 2015), to improve reproducibility and standardisation, these steps are not well suited specifically for investigating the release of Fe(II) from ash. Herein we therefore adopt ash:solute ratios comparable to the lower end of the range used in leaching experiments and comparable to the range used in incubation experiments. Seawater was used after prolonged storage in the dark (to reduce biological activity to low background levels) and without UV treatment (to maintain an environmentally relevant level of natural organic material in solution). A short leaching time (10 minutes + filtration) was adopted to minimize bottle effects and recognising that most prior work suggests a large fraction of Fe release occurs on short timescales (minutes), followed by more gradual changes on timescales of hours to days (Duggen et al., 2007; Frogner et al., 2001; Jones and Gislason, 2008).

A variety of leaches were conducted in de-ionized water, brackish (fjord) water or offshore South Atlantic seawater (Table 1) with the choice of leaching conditions based on the expected environmental significance in different water masses. Offshore oligotrophic seawater for incubation experiments was collected from an underway transect of the mid-South Atlantic (across 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. and was filtered (AcroPak1000 capsule 0.8/0.2 µm filters) when subsampling a batch for use in all 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-

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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, selected to be environmentally relevant and comparable to prior incubation experiments, 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 concentrated 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 with continuous in-line analysis (5-7°C see Sup. Table 2) 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~~For these experiments, a pre-weighed mass of ash was added to 250 ml South Atlantic seawater and manually shaken for approximately one minute~~. Ash loadings ranged~~, using an expanded loading range from 0.2-4000 mg L^{-1}. Fe(II) was 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.

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Reported mean values (± standard deviation) are determined from the Fe(II) concentrations measured 2-30 minutes after adding ash into solution. Calibrations were run daily using standard additions of 0.2-10 nM Fe(II) to aged South Atlantic seawater at the same temperature with integrated peak area used to construct calibration curves. Following each leaching experiment 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. Fe(II) leaches 2 weeks after the eruption were run for 30 minutes. Fe(II) leaches after 4 or 9 months were run for 1 hour to further investigate the temporal development of Fe(II) concentration. The trace metal leach experiments (above) were conducted at the same time as the first Fe(II) incubation experiments (2 weeks after ash collection).

For trace metal leaches, the initial (mean ± standard deviation) dissolved trace metal concentrations were deducted from the final concentrations, in order to 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.

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2.3 Ash samples – de-ionized and brackish water leaching experiments

Fresh brackish sub-surface water from the Patagonia study region was obtained from the Aysén Fjord, at Ensenada Baja (45º21'S: 72º40'W, salinity 16.3), close to the Coyhaique laboratory (Aysén region, Chile) and free from the influence of ash from the 2015 eruption. The oceanographic conditions in these waters are similar to the adjacent Reloncaví fjord

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~~(Cáceres et al., 2002; González et al., 2011). De-ionized water, along with the Aysén fjord brackish water, were used for leaching experiments following recommendations of Witham et al., (2005).~~(Cáceres et al., 2002). De-ionized water, along with the Aysén fjord brackish water, were used for leaching experiments using two size fractions of ash following the general recommendations of Duggen et al., (2010) and Witham et al., (2005) to consider the effects of different size fractions and leachates. Leaches were conducted in 50 ml LDPE bottles filled with either 40 ml brackish or 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 ~~size~~mass distribution of the ash as determined by sieving was 4.54% >2360 µm; 6.85% <-2360 µm and >1000 µm; 31.12% <1000 µm and >250 µm; 24.14% <250 µm and >125 µm; 18.04% <125 µm and >63 µm; 15.31% <63 µm.

The dominant size fraction by mass was thereby the 250-1000 µm fraction which was analyzed in addition to the finest fraction (<63 µm) with the greatest surface area to mass ratio. 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. Leaching experiments conducted with brackish water were analyzed for total alkalinity (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 (American Public Health Association) 2005-Methods 2320 (2320 Alkalinity, titration method). Additional 5 ml subsamples were filtered, stored at 4°C and

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analyzed within 3 days for major ions (~~Fl~~F^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-}, Li^{+}, Na^{+}, NH_4^{+}, K^{+}, Mg^{2+}, Ca^{2+}) using a DionexTM 5000 Ion Chromatography system with Eluent Generation (APHA). All measurements were then corrected for initial water concentrations prior to ash addition. Saturation indices for species in solution following leaching from <63 µm ash particles were obtained from the MINTEQ 3.1. IAP Ion Activity Product chemical equilibrium model (see Sup. Table 6).

Table 1. Summary of different leaching experiments and samples.

Ash/ particle source	~~Experiment type-objective~~De-ionized water leaches	Brackish (fjord) water	South Atlantic seawater	Nº of replicates
~~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~~macronutrients	Total alkalinity	-	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~~macronutrients	Total alkalinity	-	4
~~Calbuco Volcanic ash, unsieved~~	~~Trace metal leaches, S Atlantic seawater~~			~~3~~

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Calbuco ~~Volcanic~~ ash, unsieved	-	-	Trace metals, Fe(II) ~~leaches, chilled S Atlantic seawater~~	~~1*~~3 for trace elements, 1 time series for Fe(II)

~~*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 surface and at~~ 3 m depth ~~for pCO_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, as per Vergara-Jara et al., (2019). Sensor maintenance and quality control is described by Vergara-Jara et al., (2019). The error in pCO_2 concentrations is estimated to be at most 5% which arises mainly due to a non-linear sensor response and reduced sensitivity at high pCO_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

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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).

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 at 3 stations (A, B and C; Fig. 1) using a 5 L Go-Flo bottle. Samples were analyzed using ~~a~~an 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,~~1), chlorophyll-a samples were retained from 6 depths (1, 3, 5, 7, 10 and 15 m~~).~~) on 6 occasions during March-May 2015. Chlorophyll-a was determined by fluorometry after filtering 250 ml of sampled water through GFF filters (Whatman)~~ by fluorometry~~ as per ~~Welschmeyer (1994).~~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}) were determined to 15 m depth. ~~Chlorophyll-a within Reloncaví Fjord is invariably concentrated in the upper ~10 m (González et al., 2010; Yevenes et al., 2019)~~Chlorophyll-a within Reloncaví Fjord is invariably concentrated in the upper ~10 m (González et al., 2010; Yevenes et al., 2019) and thus, for comparison to prior ~~data~~ reported data integrated to 10 m, only a small difference is anticipated. For all profiles considered herein~~ (Fig. 4),~~ there is a

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20% difference between integrating to 10 m or 15 m depth.

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).~~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 the UV Aerosol Index largely reflects strongly UV-absorbing (dust) aerosols (Torres et al., 2007), this was used 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.

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) (Van Eaton et al., 2016; Reckziegel et al., 2016; Romero 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).

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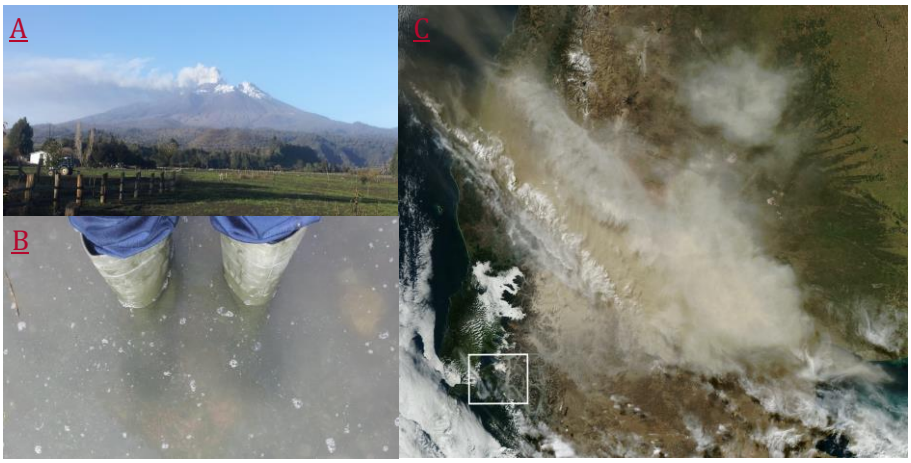

Figure 2. A Calbuco volcano ash plume 6 May ~~6~~ 2015. B Reloncaví Fjord water with atypical high turbidity due to the ash loading, Cochamó town 6 May ~~2015~~. C Ash cloud visible on MODIS Aqua satellite from the NASA Earth Observatory, 23 April ~~23~~ (~~http://earthobservatory.nasa.gov/NaturalHazards/view.php?id=85767&eocn=home&eoci=nh~~http://earthobservato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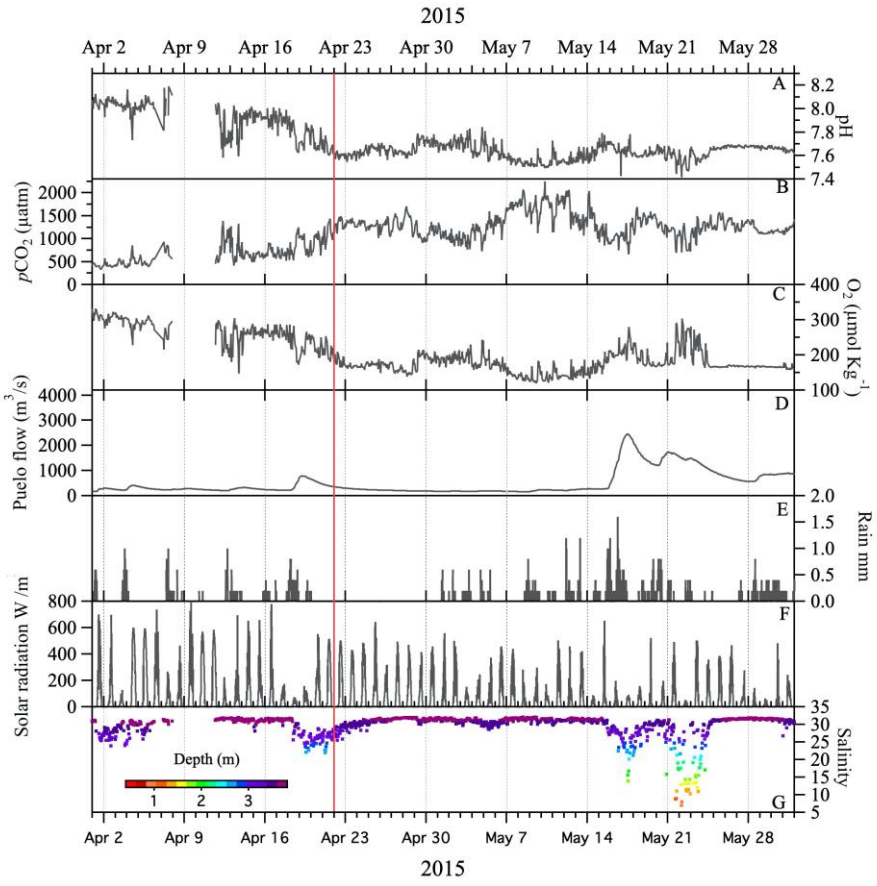

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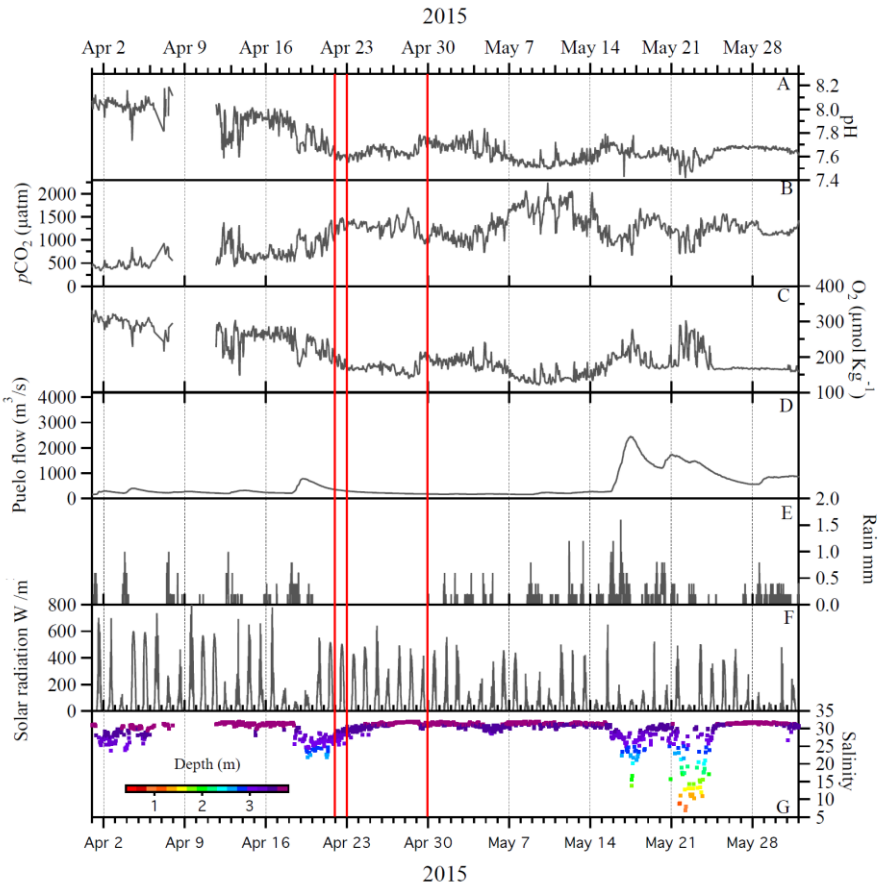

Figure 3. Continuous data from the Reloncaví Fjord mooring and nearby hydrological and weather stations for April-May 2015. The vertical red ~~line marks~~lines mark the eruption ~~date~~dates. All locations are marked in Fig 1. Carbonate chemistry and salinity data from Vergara-Jara et al., (2019).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

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Carbonate chemistry data from the Reloncaví Fjord mooring demonstrated that pH declined and pCO_2 increased in the week prior to the first eruption (22 April, Fig. 3). Oxygen and pH reached a minimum and pCO_2 a maximum during the time period ~~May~~ 7-14 May, which indicates a state of high respiration. In this stratified environment, the brackish fjord surface layer has 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 varied 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~~eruptions, or associated ash deposition, are therefore challenging to distinguish from background variation due to 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 16 May ~~16~~ which is an annually recurring event (González et al., 2010).

3.2 Phytoplankton in Reloncaví fjord post-eruption

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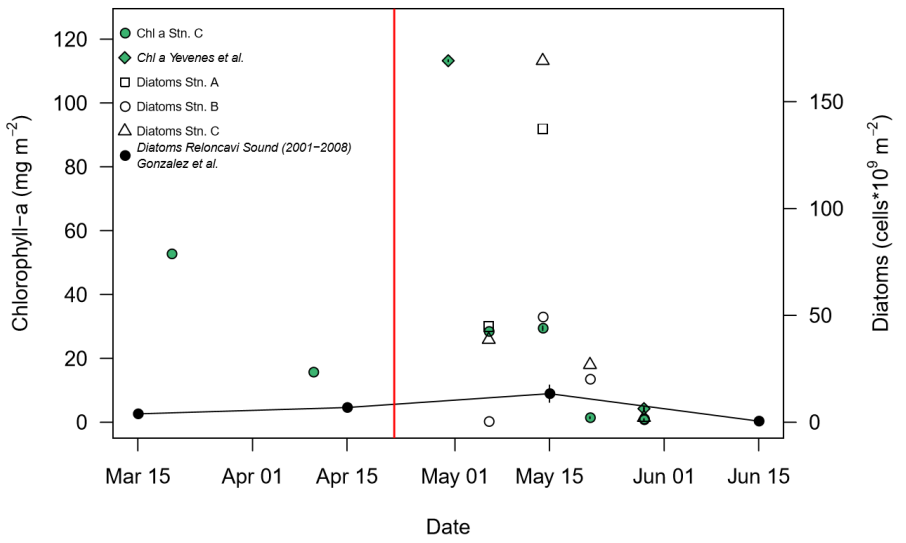

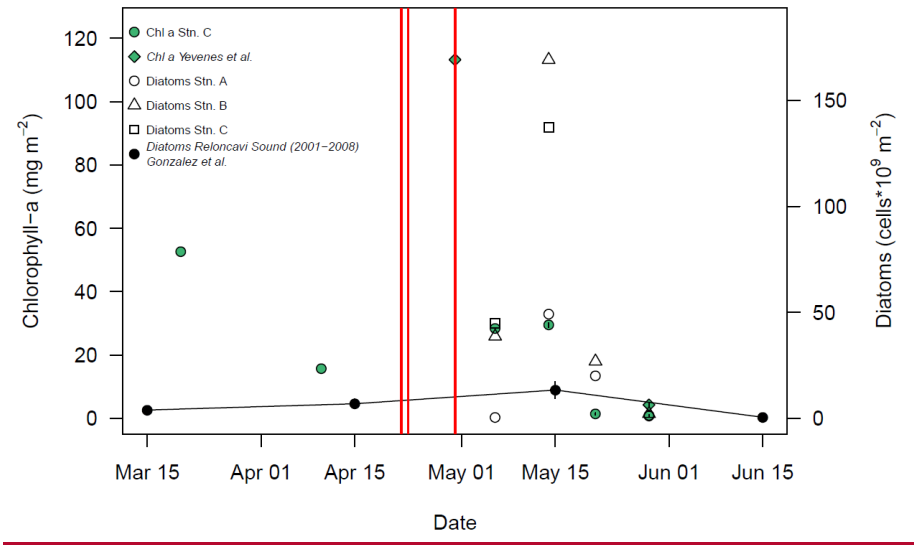

Figure 4. Changes in integrated (0-15 m) diatom abundance and chlorophyll-a for Reloncaví Fjord in April-May 2015. Locations as per Fig. 1, the eruption ~~date (22 April) is~~dates are marked with ~~a~~red lines. Historical diatom data from Reloncaví Sound (2001-2008, integrated

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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.~~

) 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 (Sup. Table 3) and were proportionate to, or higher than, those previously observed in the region (Fig. 4). When comparing observations to prior data from ~~González et al., (2010)~~ González et al., (2010) 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. Diatom abundance integrated to 15 m depth peaked at Stations ~~A~~B and C around ~~14th~~14 May, with notably lower abundances at the ~~more freshwater influenced~~innermost station ~~B~~A (Fig. 4~~), located at a mid-fjord site between the 3 major river outflows.~~). The highest measured chlorophyll-a concentrations were on ~~30th~~30 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). 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~~eruptions from the available chlorophyll-a or diatom data. Within this

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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.

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~~larger ash-particles ~~(>1.0 mm~~(250-1000 µm) no effect was 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 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.

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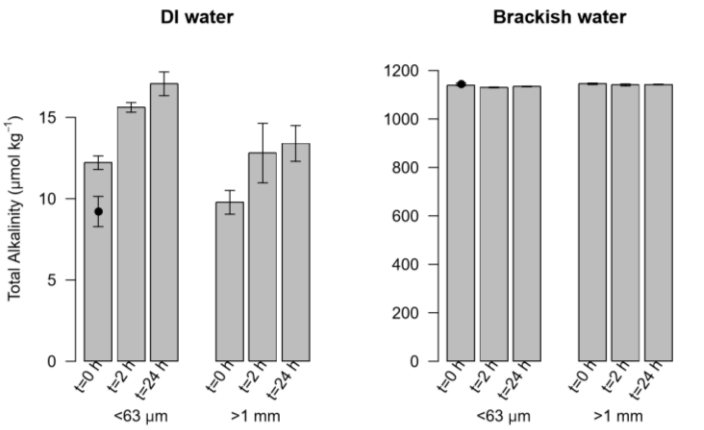

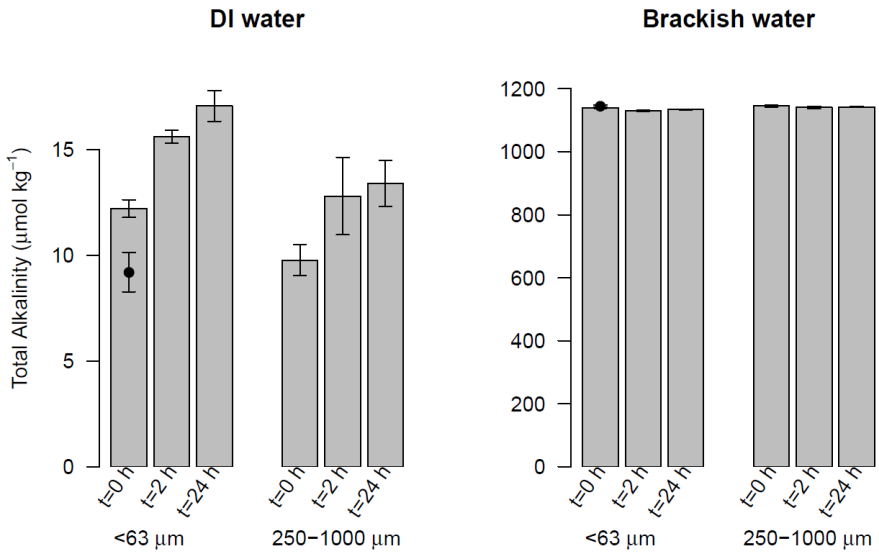

Figure 5. Total alkalinity released after leaching 4.5 g L^{-1} ash of two size fractions (<63 µm and ~~>1.0 mm~~250-1000 µm) in de-ionized water (DI water) and brackish water. T_0= 'time zero', measured after one minute of mixing, T_{2H}= after two hours of mixing, T_{24H}= after 24 hours of mixing. n=4 for all treatments (mean ± standard deviation plotted). The initial (pre-

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ash addition) alkalinity is marked by a black dot superimposed on the left T_0. Source data is provided in Supplementary Table 4.

~~Ion chromatography 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. The 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 2). 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). The concentrations of NO_3 and NH_4 were generally below detection suggesting that ash was a minor source of these 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).~~

Ion chromatography results for Na^+, K^+, Ca^{2+}, F^-, Cl^-, NO_3^- and SO_4^{2-} showed that in the presence of smaller ash size particles, ion inputs were generally higher (Table 2) as has been reported previously (Jones and Gislason, 2008; Óskarsson, 1980; Rubin et al., 1994). The 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 2). For larger particles there was less release of most ions. In the case of Ca^{2+} and SO_4^{2-} a more gradual leaching effect was apparent (Table 2). The concentrations of NO_3^- and NH_4^+ were generally below detection suggesting that ash was a minor source of fixed-nitrogen into solution. These observations are consistent with the trends in prior work using a range of volcanic ash and incubation conditions (Duggen et al., 2010; Witham et al., 2005). Major ion analysis was

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only conducted in de-ionized water as no significant changes would be observable for most of these ions in brackish or saline waters under the same conditions.

	Time [h]	**Na^+**	**K^+**	**Ca^{2+}**	**~~FI~~F^-**	**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~~ 250-1000 µm [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

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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).~~ 250-1000 µm) 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 was evident when ash was re-suspended in aged seawater for 10 minutes (Fig. 6). The net release of dissolved metals proceeded with varying relationships with ash loading over the applied gradient (~~0.1 – 6~~2-50 mg L^{-1}). Dissolved Mn, Pb, Cu and Co release exhibited significant ($p < 0.05$) positive

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relationships with ash loading, with Mn and Cu exhibiting the most linear behavior (R^2 0.99 and 0.83, respectively). Dissolved Fe, Cd and Ni showed no significant relationships with ash loading over the applied range. 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~~,~~ (Fe, Co and Pb), non-linearity between ash addition and trace metal concentrations, and some negative changes in concentrations, 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. The divergence between the behaviour of Mn and Fe, with Mn showing a stronger relationship with ash loading, supports the hypothesis of Mendez et al., (2010), that the release of dissolved Mn from aerosols into seawater depends primarily on ash Mn availability whereas the release of dissolved Fe is more dependent on the nature of organic material present in solution.

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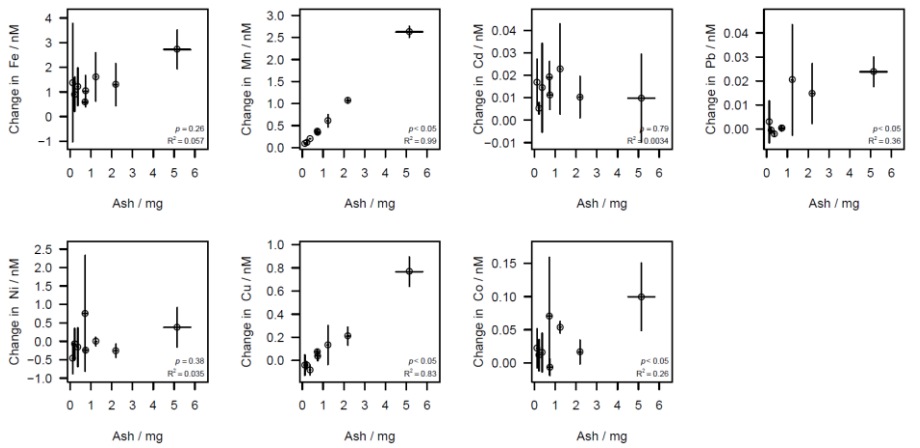

Figure 6. Change in trace metal concentrations after varying ash addition to 100 ml South Atlantic seawater for a 10-minute leach duration at room temperature. Initial (mean ± standard deviation) dissolved trace metal concentrations - deducted from the final concentrations to calculate the change as 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 values and R^2 for a linear regression are annotated. Source data is provided in Supplementary Table 5. The same data with individual replicates is shown in Supplementary Figure 1.

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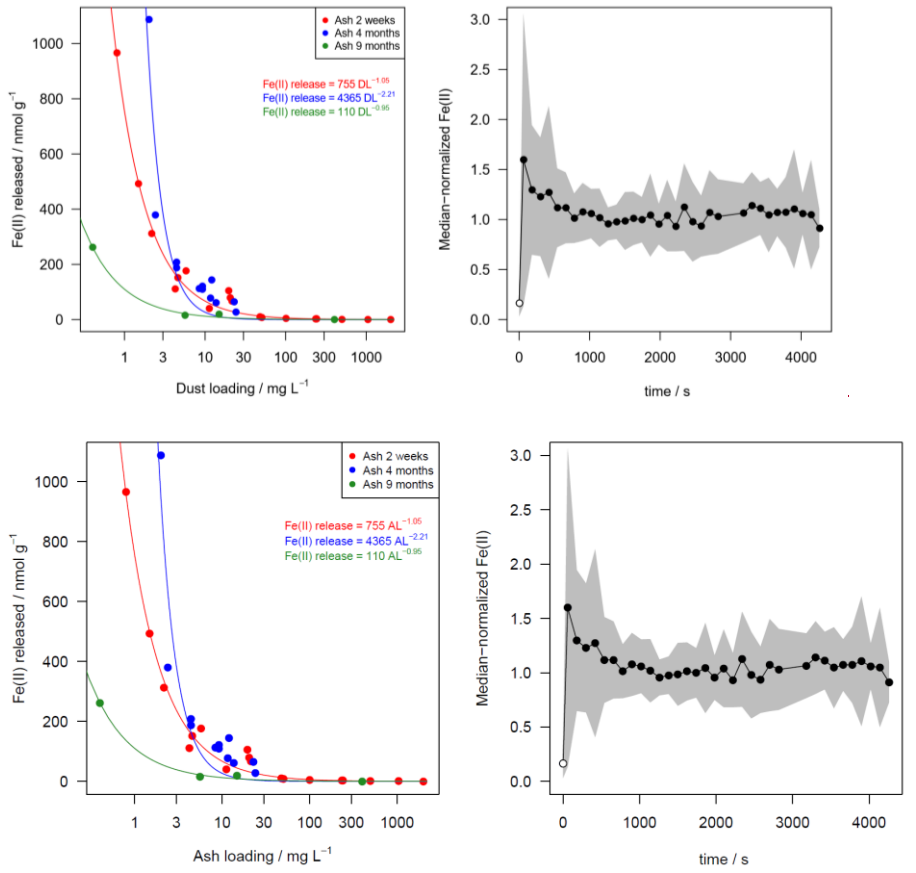

Figure 7. Fe(II) release from Calbuco ash into seawater. Mean Fe(II) released into South Atlantic seawater over a 30 minute leach at 5-7°C (left). The same batch of Calbuco ash was subsampled and used to conduct experiments on 3 occasions after the 2015 eruption (2 weeks, 4 months and 9 months since ash collection). The ~~30 minute~~lines are power law fits, with associated equations shown in the legend. The 3 time-series of Fe(II) concentrations following ash addition ~~are~~is considered collectively by normalizing the measured concentrations (right), such that 1.0 represents the median Fe(II) concentration measured in

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each experiment ~~2 30 minutes after ash addition.~~. All experiments were conducted for at least 30 minutes, those conducted with 4/9 months old ash were extended for 1 hour. 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). Source data is provided in Supplementary Table 2.

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 Fe(II) concentrations ~~of up to 4.~~(mean 0.8 nM ~~Fe(II,~~ Sup. Table 2) were evident at this temperature (5-7°C), which represents an intermediate sea surface temperature for the high latitude ocean. 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 observed at the lowest ash loading (Fig. ~~7~~7 and Sup. Fig. 2). Fe(II) concentration following dust addition into seawater was possibly 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 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.

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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 (Fig. 7).

3.5 Satellite observations

Five-day composite images of atmospheric aerosol loading (UV aerosol index~~) indicated two main volcanic eruption plume trajectories~~, which largely represents strongly UV-absorbing dust, Torres et al., 2007) indicated two main volcanic eruption plume trajectories following the major eruptions on 22 and 23 April: (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~~.~~ (Sup. Fig. 3).

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

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area to the south of the Rio de la Plata (Sup. Fig. 3), 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., 2014; Duggen et al., 2007; Mélançon et al., 2014)~~(Browning et al., 2014; Duggen et al., 2007; Mélançon et al., 2014).

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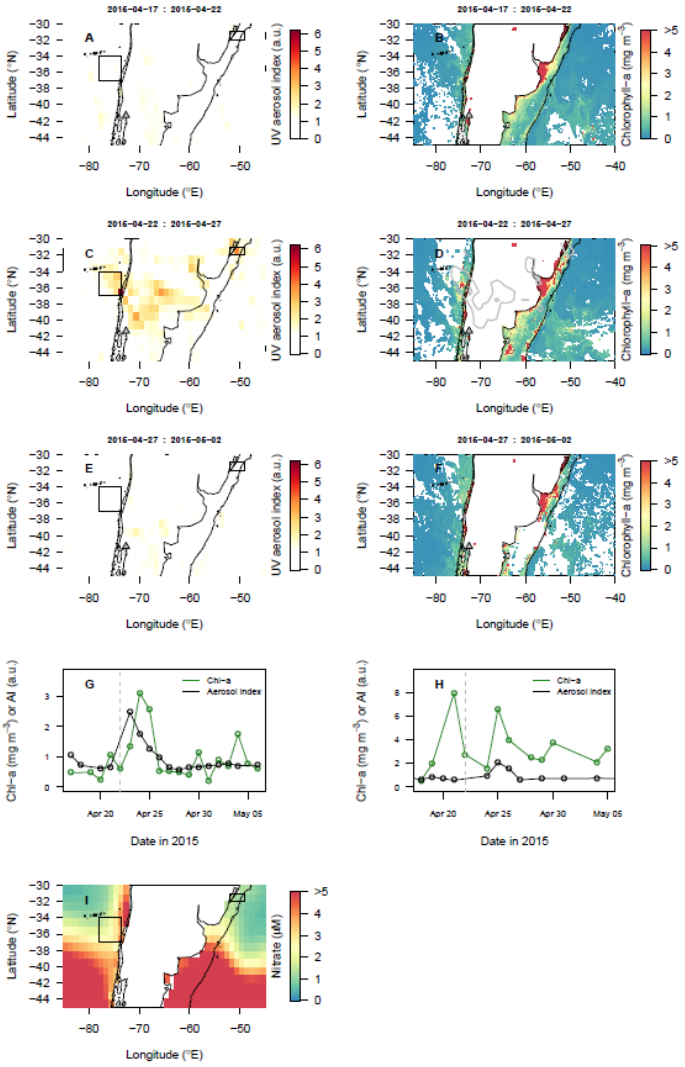

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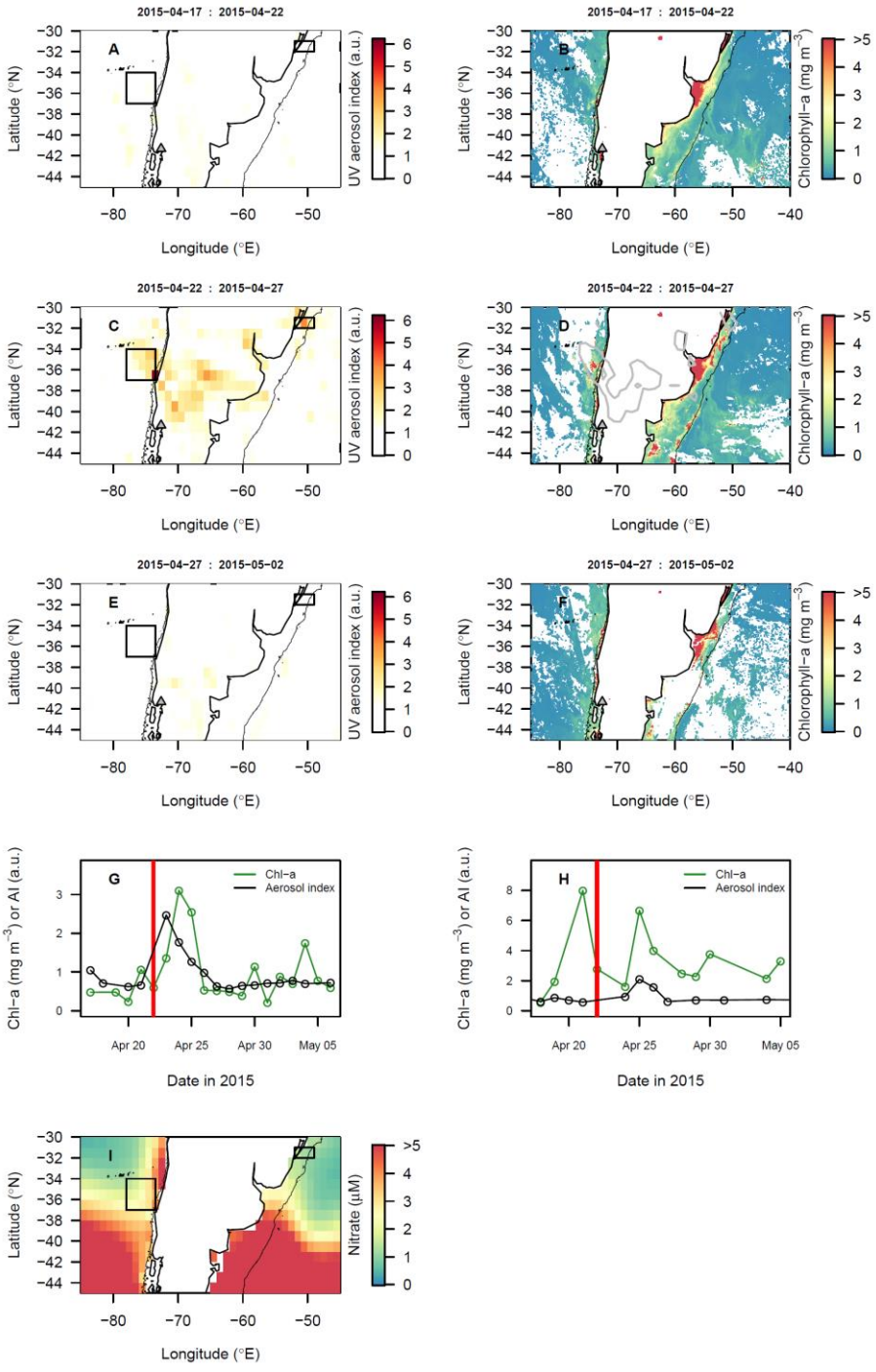

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Figure 8. Potential biological impact of the 2015 Calbuco eruption observed via satellite remote sensing. (A-F) Spatial maps showing the distribution of ash in the atmosphere (UV Aerosol Index) and corresponding images of chlorophyll-a. Images were 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~~Red vertical lines (22 April) indicate the first 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~~deposition events, 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

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603 respect to the timing of the phytoplankton bloom, the low diatom abundances and
604 chlorophyll-a concentrations at the end of May (Fig. 4) are consistent with prior observations
605 of sharp declines in primary production moving into June (González et al., 2010). Peaks in
606 diatom abundance were measured at two stations on ~~14th~~14 May one week after the third
607 (small) eruptive pulse, and measured chlorophyll-a concentrations were highest close to
608 Station C on 30 April (Fig. 4). The high-resolution pH and O_2 data collected at Station C
609 from mooring data is consistent with an intense phytoplankton bloom between ~29 April and
610 7 May (Fig. 3) indicated by a shift to slightly higher pH and O_2 during this time period when
611 river flow into the fjord was stable.
612
613 Without a direct measure of ash deposition per unit area in the fjord, turbidity, or higher
614 resolution chlorophyll/diatom data, it is challenging to unambiguously determine the extent
615 to which the austral autumn phytoplankton bloom was affected by volcanic activity. The high
616 abundance of diatoms at two of three stations sampled could have resulted from ash
617 fertilization. Yet if this was the case, it is not clear which nutrient was responsible for this
618 fertilization, why the bloom initiation occurred about one week after the third eruptive pulse
619 (several weeks after the main eruption~~,~~ events) and to what extent the timing was coincidental
620 given that productivity normally peaks in May. Reloncaví Fjord was to the south of the
621 dominant ash deposition from the 22 and 23 April eruptions (Romero et al., 2016)~~. Both~~
622 ~~runoff and rainfall were vectors by which ash was deposited in the fjord, which~~ and thus ash
623 was delivered by a mixture of vectors including runoff and rainfall. The Petrohue river basin
624 was particularly severely affected by ash with deposition of up to 50 cm ash in places. This
625 complicates the interpretation of the time series provided by high resolution data (Fig. 3).

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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 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 plausibly explain higher than usual diatom abundance (Siringan et al., 2018). Silicic acid concentrations were indeed high (up to ~~80~~118 µM) in Reloncaví Fjord surface waters ~~in May 2015~~and >30 µM at 15 m depth (salinity 33.4) ~~(Yevenes et al., 2019), however concentrations in excess of~~ (Vergara-Jara et al., 2019; Yevenes et al., 2019). However concentrations >30 µM are typical during periods of high

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runoff and accordingly are not thought to limit primary production or diatom growth in this area (González et al., 2010). The $Si(OH)_4$:NO_3 ratio in Reloncaví Fjord and downstream Reloncaví Sound also indicates an excess of $Si(OH)_4$, 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 silicic acid only when $Si(OH)_4$ and NO_3 were added in combination, further corroborating the hypothesis that an excess of silicic acid 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

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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 main 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). Fe(II) release was particularly efficient at ash loadings <5 mg L^{-1} (Fig. 7)~~). For dFe this is comparable to the rates determined in other studies under similar experimental conditions for subduction zone volcanic ash, with reported Fe-release in prior work ranging 2-570 nmol g^{-1} (Sup. Table 1). For Mn, less prior work is available, but these values are within the 17-1300 nmol g^{-1} range reported by Hoffmann et al., (2012). 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

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process. Fe(II) is short lived in oxic surface seawater with an observed half-life of only 10-20 minutes even in the Southern Ocean where cold surface waters 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). 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 dFe 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. Prior work, at much lower pH (pH 1 H_2SO_4 representing conditions that ash surfaces may experience during atmospheric processing, but not in aquatic environments) suggests that short-term release of Fe(II) or Fe(III) is determined by the surface Fe(II)/Fe ratio which may differ from the bulk Fe(II)/Fe ratio due to plume processing (Maters et al., 2017).

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., 2007; Morton et al., 2013). When Fe(II) is released into solution as a considerable fraction of the total dFe release this is particularly challenging to monitor, as Fe(II) oxidises on timescales of seconds to minutes depending on temperature, pH and O_2 conditions (Santana-Casiano et al., 2005). The dFe and Fe(II) leaching protocols used herein are only comparable

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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 across zonal transects of the Pacific Ocean (Buck et al., 2013) suggesting that fresh Calbuco 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). Following the eruption date, mean chlorophyll-a concentrations increased ~2.5 times over a broad region where elevated UV aerosol index 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

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changes in chlorophyll-a matching that observed in the higher UV aerosol index region to the north (Sup. Fig. 3).

In the SW Atlantic, two ash impacted areas are highlighted; one to the north (Fig. 8), and one to the south of the Rio de la Plata (Sup. Fig. 3). Nitrate levels are expected to be higher in the south than to the north, with Fe levels expected to be elevated across both locations as a result of their position on the continental shelf. In the area to the north of the Rio de la Plata (Fig. 8), ash deposition 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., ~~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. 3). 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 likely peaked much later than the first ash arrival after 28 April. The fertilized region of the Pacific (Fig.~~ whilst also being proceeded by a larger chlorophyll-a peak on 21 April, there is a peak in chlorophyll-a at 25 April coinciding with elevated UV aerosol index). Phytoplankton growth in this region of the Atlantic is

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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 alone would not be expected to result in short-term increases to primary production. In the second area of ash deposition, to the south (Sup. Fig. 3), 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. 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 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 coinciding with elevated UV aerosol index). 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

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787 Atlantic are therefore consistent with the anticipated nutrient limitation regimes (Fe-limited
788 and nitrogen-limited, respectively), and the supply of dFe but not fixed N (NO_3 or NH_4) from
789 the Calbuco ash (Fig. 6 and Table 2).
790
791 **5 Conclusions**
792 The contrasting effects of volcanic ash on primary producers in Reloncaví Fjord, the SE
793 Pacific and SW Atlantic Oceans support the hypothesis that the response of primary
794 producers is dependent on both the ash loading and the resources limiting primary production
795 in a region at a specific time of year. Leach experiments using ash from the 2015 Calbuco
796 eruption demonstrated a small increase in the alkalinity of de-ionized water from fine, but
797 not coarse ash, and no significant addition of fixed nitrogen (quantified as NO_3 and NH_4) into
798 solution. In saline waters, release of dissolved trace metals including Mn, Cu, Co, Pb, Fe and
799 specifically Fe(II) was evident.
800
801 Strong evidence of a broad-scale 'bottom-up' fertilization effect of ash on primary production
802 was not found locally within Reloncaví Fjord, although it is possible that the timing and peak
803 diatom abundance of the autumn phytoplankton bloom may have shifted in response to high
804 ash loading in the weeks following the first eruption. High diatom abundances at some
805 stations within the fjord several weeks after the eruption may have arisen from a 'top-down'
806 effect of ash on filter feeders, although the mechanism can only be speculated herein. No
807 clear positive effect of ash deposition on chlorophyll-a was evident in the SW Atlantic,
808 consistent with expected patterns in nutrient deficiency which suggest the region to be
809 nitrogen-limited. However, in offshore waters of the SE Pacific where Fe is anticipated to

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limit phytoplankton growth, a chlorophyll-a increase was related with maximum ash deposition and we presume that this 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

The authors thank the Dirección de Investigación & Desarrollo UACh for its partial support during this project. The data presented are part of the second chapter of the PhD Thesis of MVJ at Universidad Austral de Chile. Cristian Vargas (Universidad de Concepción) is thanked for making additional chlorophyll a data available, Manuel Díaz for providing Fig. 1 ~~and~~, Lorena Rebolledo for running the particle size test, Miriam Beck for assistance with Fe(II) flow injection analysis and 3 reviewers for constructive comments that improved the manuscript.

8. Funding

JLI and EA gratefully acknowledge funding from the European Commission (OCEAN-CERTAIN, FP7- ENV- 2013-6.1-1; no: 603773). JLI received funding by CONICYT-FONDECYT 1141065 and is partially funded by Center IDEAL (FONDAP 15150003). Partial funding came from CONICYT-FONDECYT 1140385 (RT). MVJ received financial

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833 support from a CONICYT Scholarship (Beca Doctorado Nacional 2015 No 21150285). IR
834 and MH received funding from the Deutsche Forschungsgemeinschaft as part of
835 Sonderforschungsbereich (SFB) 754: 'Climate-Biogeochemistry Interactions in the Tropical
836 Ocean'.
837
838 **9. Author contributions**
839 MVJ, MH, JLI and EA designed the study. MVJ, IR, MH, RT and BR conducted analytical
840 and field work. TB conducted satellite data analysis. MV, MH and TB wrote the initial
841 manuscript with all authors contributing to its revision.
842
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