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

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Supplementary Material

Reference	Method	Duration	Samples	Ash size	Ash/solute ratio (g:mL)	Solute	dFe* release nmol Fe /g
Frogner et al., 2001	Flow-through reactor	8 h	Hekla	45-74 µm	1:8	Artificial and Atlantic seawater	37000-39000 (45 min)
Duggen et al., 2007	Stripping voltammetry	1 h	Pacific selection	unsieved	1:400	Antarctic seawater	18-72(1 h)
Jones and Gislason, 2008	Flow-through reactor	24 h	Global selection	45-125 µm	1:8	Atlantic and Southern Ocean seawater	10-8900
Olgun et al., 2011	Stripping voltammetry	1 h	Global selection	unsieved	1:400	Atlantic seawater	35-340
Olgun et al., 2013b	Stripping voltammetry	1-24 h	Etna	unsieved	1:50	Atlantic seawater	11-130
Hoffmann et al., 2012	Suspension experiment	15 minutes	Pacific	unsieved	1:375	Seawater	2-83
Olgun et al., 2013a	Stripping voltammetry	1 h	Kasatochi	< 2 mm	1:400	Seawater	61-83

Zhang et al., 2017	Suspension experiment	12 h	Eyjafjallajökull	unsieved	1:400	Seawater	12000
Simonella et al., 2015	Stripping voltammetry	1-2 h	Andes	< 63 µm	1:2000	Patagonia seawater	64-570
Herein	Suspension experiment	10 minutes	Calbuco	unsieved	1:200 – 1:5000000	Atlantic seawater	53 - 1200

Supplementary Table 1 Summary of prior work conducting leaching experiments with volcanic ash in seawater. *****Note the definition of dFe varies between studies based on varying filtration practices and analytical techniques.

Sample type	Origin	T °C	Mean concentration of Fe(II) nM	SD nM	Particle loading mg l^{-1}
Volcanic ash	Calbuco ash (aged 2 weeks)	5.8	1.43	0.19	21.4
Volcanic ash	Calbuco ash (aged 2 weeks)	5.8	1.61	0.38	20.4
Volcanic ash	Calbuco ash (aged 2 weeks)	5.8	2.04	0.45	19.5
Volcanic ash	Calbuco ash (aged 2 weeks)	5.6	0.38	0.058	50.3
Volcanic ash	Calbuco ash (aged 2 weeks)	5.6	0.47	0.11	4.2
Volcanic ash	Calbuco ash (aged 2 weeks)	5.6	0.48	0.1	47.7
Volcanic ash	Calbuco ash (aged 2 weeks)	5.6	0.43	0.16	100.3
Volcanic ash	Calbuco ash (aged 2 weeks)	5.6	0.30	0.11	495.7
Volcanic ash	Calbuco ash (aged 2 weeks)	5.6	0.20	0.084	1040.8
Volcanic ash	Calbuco ash (aged 2 weeks)	5.6	0.15	0.0474	1997.4
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.45	0.0457	11.2
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	1.02	0.817	5.8
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.69	0.205	4.6
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.67	0.106	2.2
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.73	0.136	1.5
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.77	0.118	0.8
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.57	0.150	234.0
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.71	0.220	238.9
Volcanic ash	Calbuco ash (aged 2 weeks)	5.7	0.63	0.118	240.4
Volcanic ash	Calbuco ash (aged 4 months)	5.7	0.65	0.101	24.0
Volcanic ash	Calbuco ash (aged 4 months)	5.7	1.72	3.15	12.0

Volcanic ash	Calbuco ash (aged 4 months)	5.7	0.94	0.156	8.4
Volcanic ash	Calbuco ash (aged 4 months)	5.7	0.91	0.0840	4.4
Volcanic ash	Calbuco ash (aged 4 months)	5.7	2.17	1.07	2.0
Volcanic ash	Calbuco ash (aged 4 months)	5.7	1.47	0.326	22.8
Volcanic ash	Calbuco ash (aged 4 months)	5.7	0.83	0.137	13.6
Volcanic ash	Calbuco ash (aged 4 months)	6.7	1.11	0.176	9.2
Volcanic ash	Calbuco ash (aged 4 months)	6.7	0.82	0.335	4.4
Volcanic ash	Calbuco ash (aged 4 months)	6.7	0.91	0.112	2.4
Volcanic ash	Calbuco ash (aged 4 months)	6.7	0.90	0.0943	11.6
Volcanic ash	Calbuco ash (aged 4 months)	6.7	1.01	0.111	9.2
Volcanic ash	Calbuco ash (aged 9 months)	7.2	0.29	0.0914	14.8
Volcanic ash	Calbuco ash (aged 9 months)	7.2	0.10	0.137	0.4
Volcanic ash	Calbuco ash (aged 9 months)	7.2	0.044	0.122	400
Volcanic ash	Calbuco ash (aged 9 months)	7.2	0.087	0.192	5.6

Supplementary Table 2. Fe(II) leaching experiments conducted Calbuco ash at different time intervals. SD standard deviation. T, temperature.

Date	Chlorophyll-a mg m^{-2}	Diatoms cells m^{-2} ($\times 10^{-6}$) Station A	Diatoms cells m^{-2} ($\times 10^{-6}$) Station B	Diatoms cells m^{-2} ($\times 10^{-6}$) Station C
3/20/2015	52.7	*n.d.*	*n.d.*	*n.d.*
4/10/2015	15.7	*n.d.*	*n.d.*	*n.d.*
5/6/2015	28.4	326	38671	44778
5/14/2015	29.4 ± 0.7	49225	169170	137289
5/21/2015	1.4 ± 0.3	20111	26904	*n.d.*
5/29/2015	0.78 ± 0.3	1569	2153	*n.d.*

Supplementary Table 3. Source data for Figure 4. Chlorophyll-a concentrations (Station C only) and diatom cell abundance (Stations A, B and C) are presented integrated to 15 m depth. Where replicate profiles were conducted for chlorophyll, the mean ± standard deviation is reported. *n.d.* no data.

Size	Water	Time (h)	A_T µmol kg^{-1}
<63 µm	De-ionized water	0	12.2 ± 0.42
<63 µm	De-ionized water	2	15.6 ± 0.30
<63 µm	De-ionized water	24	17.1 ± 0.73
1000 - 250 µm	De-ionized water	0	9.8 ± 0.73
1000 - 250 µm	De-ionized water	2	12.8 ± 1.8
1000 - 250 µm	De-ionized water	24	13.4 ± 1.1
Baseline	De-ionized water	0	9.2 ± 0.93
<63 µm	Brackish water	0	1139 ± 1.7
<63 µm	Brackish water	2	1130 ± 1.9
<63 µm	Brackish water	24	1134 ± 1.5
1000 - 250 µm	Brackish water	0	1145 ± 3.0
1000 - 250 µm	Brackish water	2	1141 ± 4.1
1000 - 250 µm	Brackish water	24	1142 ± 1.6
Baseline	Brackish water	0	1144 ± 4.6

Supplementary Table 4. Source data for Figure 5. Total alkalinity (mean ± standard deviation) from 4 replicates.

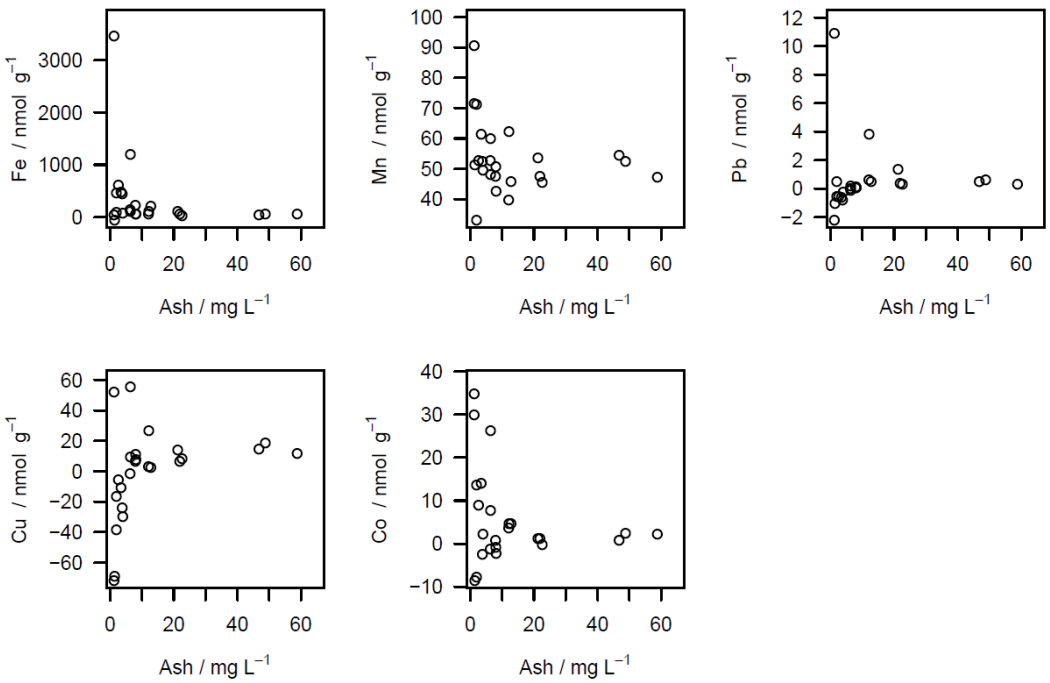
Ash / mg	ΔFe / nM	ΔCd / nM	ΔPb / nM	ΔNi / nM	ΔCu / nM	ΔCo / nM	ΔMn / nM
0.13 ±0.01	1.4 ±2.4	0.017 ±0.010	0.003 ±0.009	-0.46 ±0.41	-0.040 ±0.089	0.022 ±0.029	0.089 ±0.019
0.22 ±0.03	0.90 ±0.70	0.005 ±0.003	-0.001 ±0.001	-0.074 ±0.43	-0.042 ±0.032	0.012 ±0.024	0.12 ±0.042
0.37 ±0.03	1.2 ±0.77	0.015 ±0.020	-0.002 ±0.001	-0.16 ±0.53	-0.082 ±0.043	0.016 ±0.029	0.20 ±0.006
0.72 ±0.11	0.58 ±0.11	0.019 ±0.007	0.000 ±0.001	0.76 ±1.57	0.074 ±0.018	0.070 ±0.089	0.37 ±0.051
0.74 ±0.10	1.0 ±0.64	0.011 ±0.006	0.000 ±0.000	-0.25 ±0.075	0.037 ±0.039	-0.007 ±0.013	0.35 ±0.022
1.2 ±0.04	1.6 ±0.98	0.023 ±0.020	0.020 ±0.023	-0.005 ±0.12	0.13 ±0.17	0.054 ±0.009	0.61 ±0.14
2.2 ±0.07	1.3 ±0.86	0.010 ±0.009	0.015 ±0.012	-0.26 ±0.18	0.21 ±0.078	0.016 ±0.018	1.1 ±0.061
5.2 ±0.64	2.7 ±0.79	0.010 ±0.020	0.024 ±0.006	0.38 ±0.54	0.77 ±0.13	0.100 ±0.051	2.6 ±0.13

Supplementary Table 5. Source data for Figure 6. Change in trace metal concentrations (mean ± standard deviation) from 3 replicates.

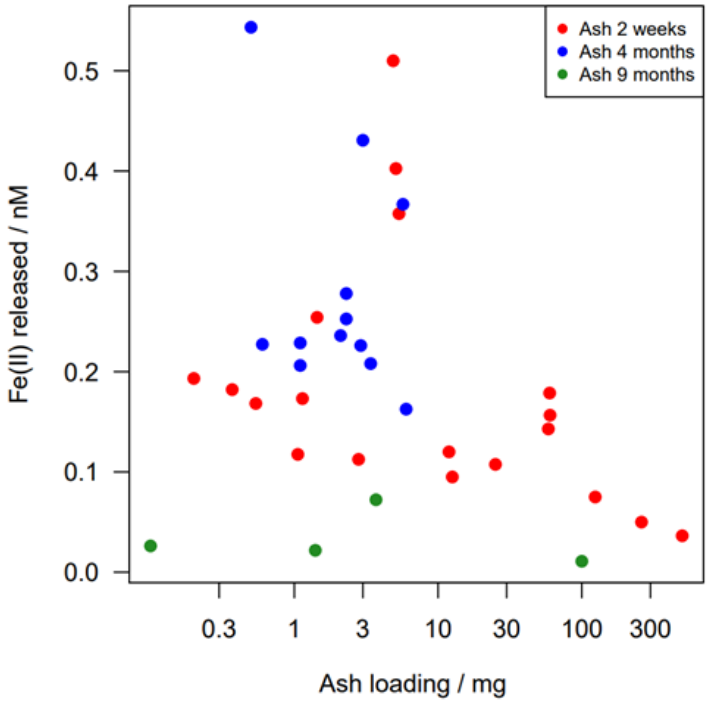
Mineral	log IAP	Saturation index
Anhydrite	-9.255	-4.939
Aragonite	-10.261	-1.982
Artinite	3.42	-6.911
Brucite	14.087	-3.706
$Ca_3(PO_4)_2$ (am1)	-32.565	-7.637
$Ca_3(PO_4)_2$ (am2)	-32.565	-4.844
$Ca_3(PO_4)_2$ (beta)	-32.565	-3.317
$Ca_4H(PO_4)_3{:}3H_2O$(s)	-56.095	-8.783
$CaCO_3xH_2O$(s)	-10.261	-3.174
$CaHPO_4$(s)	-23.53	-4.066
$CaHPO_4{:}2H_2O$(s)	-23.53	-4.395
Calcite	-10.261	-1.831
Chalcedony	-16.104	-12.434
Chrysotile	10.055	-23.337
Cristobalite	-16.104	-12.632
Dolomite (disordered)	-20.928	-4.67
Dolomite (ordered)	-20.928	-4.078
Epsomite	-9.662	-7.465

FCO_3-Apatite	-112.31	3.09
Fluorite	-16.837	-6.264
Gypsum	-9.255	-4.639
Halite	-9.61	-11.138
Huntite	-42.263	-12.95
Hydromagnesite	-28.582	-21.145
Hydroxyapatite	-41.601	2.732
KCl(s)	-10.256	-11.156
LiF(s)	-12.76	-9.962
Lime	14.494	-19.384
Magnesite	-10.667	-3.086
$Mg(OH)_2$ (active)	14.087	-4.707
$Mg_2(OH)_3Cl{:}4H_2O$(s)	13.836	-12.164
$Mg_3(PO_4)_2$(s)	-33.785	-10.505
$MgCO_3{:}5H_2O$(s)	-10.667	-6.127
MgF2(s)	-17.243	-9.182
$MgHPO_4{:}3H_2O$(s)	-23.936	-5.761
Mirabilite	-14.293	-12.696
NaF(s)	-10.937	-10.442
Natron	-15.298	-13.587
Nesquehonite	-10.667	-6.145
Periclase	14.087	-8.416
Portlandite	14.494	-8.992
Quartz	-16.104	-11.968
Sepiolite	-20.136	-36.59
Sepiolite (A)	-20.136	-38.916
SiO_2 (am, gel)	-16.104	-13.309
SiO_2 (am, ppt)	-16.104	-13.272
Struvite	-20.592	-7.332
Thenardite	-14.293	-14.67
Thermonatrite	-15.298	-15.999
Vaterite	-10.261	-2.424

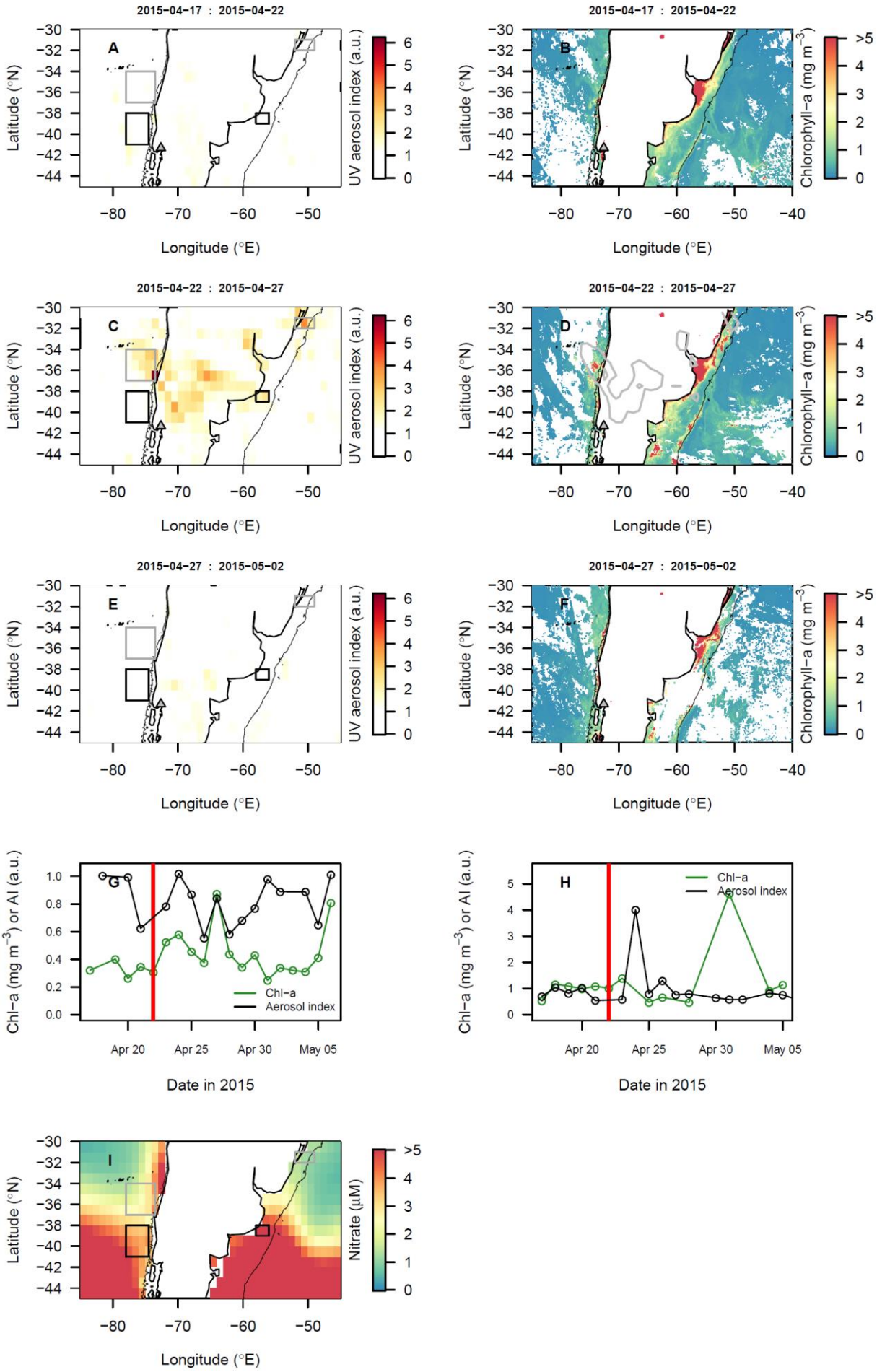
Supplementary Table 6. Results for saturation indices for species in solution regarding leaching experiment with 63 µm ash particles obtained from MINTEQ 3.1. IAP, Ion Activity Product.



Supplementary Figure 1. Change in trace metal concentration following ash addition per mass ash added. (Same data as per Figure 6 with individual replicates shown).



Supplementary Figure 2. Mean Fe(II) concentrations (2-30 minutes after ash addition) in South Atlantic seawater. (Same data as per Figure 7).


2015-04-17 : 2015-04-22
A
B
2015-04-22 : 2015-04-27
C
D
2015-04-27 : 2015-05-02
E
F
Latitude (°N)
Longitude (°E)
UV aerosol index (a.u.)
Chlorophyll-a (mg m^{-3})
G
H
Chl-a (mg m^{-3}) or AI (a.u.)
Chl-a
Aerosol index
Apr 20
Apr 25
Apr 30
May 05
Date in 2015
I
Nitrate (µM)

Supplementary Figure 3. Satellite data showing a control region on the Pacific side, and an additional site affected by ash to the south of the Rio de la Plata with their respective analysis. Thin black lines indicate the 500 m bathymetric depth contour. Grey and black boxes highlight the regions used for time series analysis in the main manuscript (Figure 8) and Supplementary Figure 3, respectively.

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