



Volcanic ash supply to the surface ocean—remote sensing of biological responses and their wider biogeochemical significance

Thomas J. Browning^{1*}, Katherine Stone¹, Heather A. Bouman¹, Tamsin A. Mather¹, David M. Pyle¹, C. Mark Moore² and Victor Martinez-Vicente³

¹ Department of Earth Sciences, University of Oxford, Oxford, UK

² Ocean and Earth Science, National Oceanography Centre Southampton, University of Southampton, Southampton, UK

³ Plymouth Marine Laboratory, Plymouth, UK

Edited by:

Maeve Carroll Lohan, University of Plymouth, UK

Reviewed by:

Kristen N. Buck, University of South Florida, USA

Mukesh Gupta, Environment Canada, Canada

*Correspondence:

Thomas J. Browning, GEOMAR Helmholtz Centre for Ocean Research, Kiel, Wischhofstraße 1-3, Build. 12, D-24148 Kiel, Germany
e-mail: tbrowning@geomar.de

† Present address:

Thomas J. Browning, GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

Transient micronutrient enrichment of the surface ocean can enhance phytoplankton growth rates and alter microbial community structure with an ensuing spectrum of biogeochemical feedbacks. Strong phytoplankton responses to micronutrients supplied by volcanic ash have been reported recently. Here we: (i) synthesize findings from these recent studies; (ii) report the results of a new remote sensing study of ash fertilization; and (iii) calculate theoretical bounds of ash-fertilized carbon export. Our synthesis highlights that phytoplankton responses to ash do not always simply mimic that of iron amendment; the exact mechanisms for this are likely biogeochemically important but are not yet well understood. Inherent optical properties of ash-loaded seawater suggest rhyolitic ash biases routine satellite chlorophyll-a estimation upwards by more than an order of magnitude for waters with <0.1 mg chlorophyll-a m^{-3} , and less than a factor of 2 for systems with >0.5 mg chlorophyll-a m^{-3} . For this reason post-ash-deposition chlorophyll-a changes in oligotrophic waters detected via standard Case 1 (open ocean) algorithms should be interpreted with caution. Remote sensing analysis of historic events with a bias less than a factor of 2 provided limited stand-alone evidence for ash-fertilization. Confounding factors were poor coverage, incoherent ash dispersal, and ambiguity ascribing biomass changes to ash supply over other potential drivers. Using current estimates of iron release and carbon export efficiencies, uncertainty bounds of ash-fertilized carbon export for three events are presented. Patagonian iron supply to the Southern Ocean from volcanic eruptions is less than that of windblown dust on 1000 year timescales but can dominate supply at shorter timescales. Reducing uncertainties in remote sensing of phytoplankton response and nutrient release from ash are avenues for enabling assessment of the oceanic response to large-scale transient nutrient enrichment.

Keywords: phytoplankton, dust, iron, ocean color, MODIS, nutrient limitation, carbon cycle, inherent optical properties

INTRODUCTION

Phytoplankton photosynthesis couples atmospheric and marine biogeochemical cycles with resultant impacts on marine food webs and climate (Falkowski et al., 1998; Kump et al., 1999; Duffy and Stachowicz, 2006; Sarmiento and Gruber, 2006). There is currently much interest and effort in constraining the supply of micronutrients, particularly iron (Fe), to marine phytoplankton (Henderson et al., 2007; Boyd and Ellwood, 2010), and resolving the biogeochemical implications of fertilization, i.e., relieving nutrient limitation (Cullen et al., 1992; Boyd et al., 2007; Moore et al., 2013). Volcanic eruptions have the potential to transiently eject thousands-to-millions of tons of fine-grained Fe-containing material high into the atmosphere in an acidic environment (e.g., Mather et al., 2003; Mason et al., 2004). The low pH of the ash

plume enhances dissolution of Fe-bearing silicate minerals within the ash particle matrix, generating Fe-rich solutions that can re-precipitate out onto the surface of ash particles as highly-soluble Fe chlorides, fluorides and sulfate salts (Delmelle et al., 2007; Duggen et al., 2010; Ayriz and Delmelle, 2012). Explosive eruptions can inject this material into the upper troposphere and stratosphere (e.g., Baines and Sparks, 2005), where it may be transported to even the remotest of open ocean regions (e.g., Self, 2006). Rapid dissolution of Fe-bearing salts can then occur on timescales less than that of ash particle settling through the photic zone of the water column (Duggen et al., 2007; Censi et al., 2010; Olgun et al., 2011).

Anomalies in atmospheric CO₂ and O₂ records in the 1990s (Keeling and Shertz, 1992; Keeling et al., 1996) were speculated

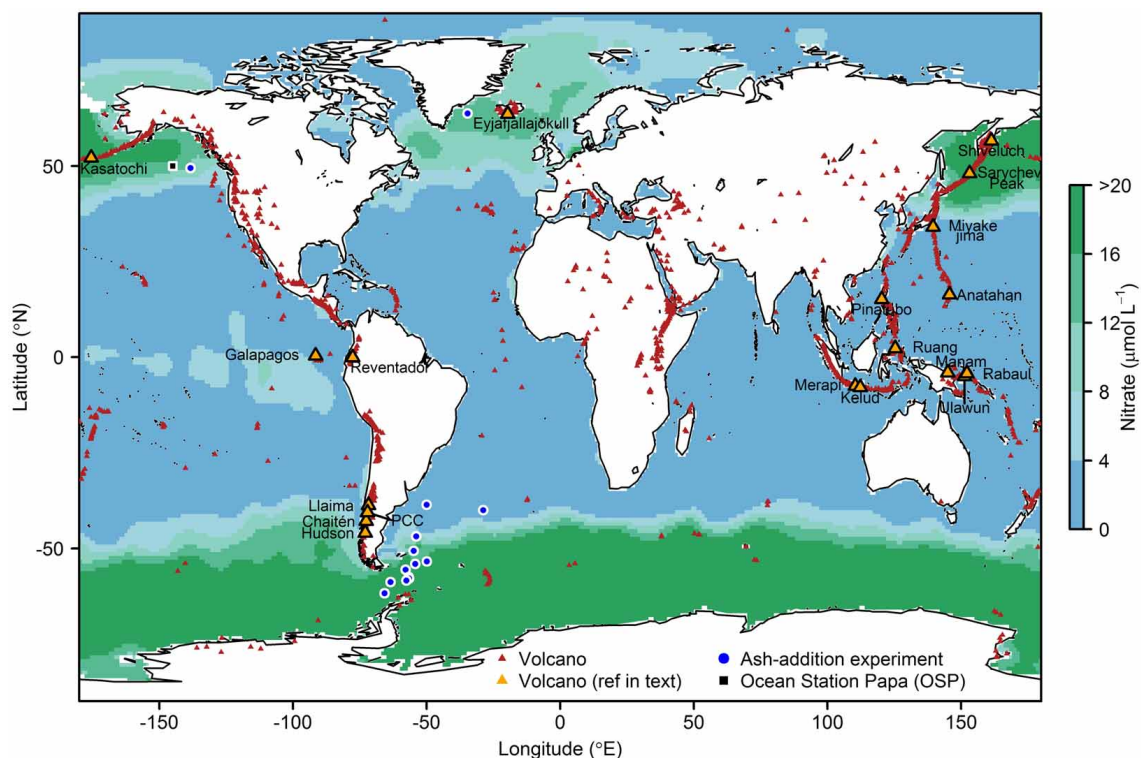


FIGURE 1 | Global surface ocean nitrate concentrations from the World Ocean Circulation Experiment (WOCE). Red triangles show the locations of volcanoes thought to have been active in the last 10,000 years (Global Volcanism Program, <http://www.volcano.si.edu/index.cfm>), orange triangles = those referred to in the main text and **Table 3**. The Sierra Negra and La Cumbre volcanoes referred to in

the text are located in the Galapagos Islands. Also shown are sites of ash addition experiments (blue circles) performed in the North Atlantic (Achterberg et al., 2013), North Pacific (Mélánçon et al., 2014) and South Atlantic and Southern Ocean (Browning et al., 2014a), and the location of Ocean Station Papa (OSP, black square). PCC, Puyehue-Cordón Caulle.

to originate from large scale Fe fertilization of the remote high-nitrate Southern Ocean after the eruption of Mt Pinatubo in 1991 (**Figure 1**; Sarmiento, 1993; Watson, 1997; after Spirakis, 1991). Unfortunately, whilst presenting an intriguing hypothesis, direct evidence for marine phytoplankton responding to ash fallout from the eruption was lacking. More recently, multiple studies have reported significant phytoplankton responses to volcanic ash supply; either following a natural deposition event (Hamme et al., 2010; Langmann et al., 2010a; Lin et al., 2011; Achterberg et al., 2013), or through controlled supply of ash to phytoplankton communities in shipboard bottle enrichment experiments (Achterberg et al., 2013; Browning et al., 2014a; Mélánçon et al., 2014).

Recent reviews have summarized progress in constraining volcanic nutrient - and in particular Fe - supply to the ocean through consideration of ash formation, atmospheric processing, and solubility experiments (Duggen et al., 2010; Ayris and Delmelle, 2012; Langmann, 2014). The aims of the current manuscript are three-fold: After briefly introducing key marine biogeochemical provinces we extend prior reviews (Duggen et al., 2010; Ayris and Delmelle, 2012; Langmann, 2014) by synthesizing phytoplankton responses to ash supply; Secondly, in conjunction with new results from experiments assessing the optical properties of rhyolitic ash suspended in seawater, we present a remote sensing analysis of

several previously unreported ash deposition events with fertilization potential; Thirdly, we calculate the uncertainty bounds of ash-fertilized carbon export for three deposition events. The biogeochemical implications of oceanic nutrient fertilization are of significant interest (Boyd et al., 2007, 2012; Sarmiento et al., 2010) and we conclude that well characterized volcanic ash deposition events could provide one such opportunistic platform for this research.

POTENTIAL FOR VOLCANIC ASH FERTILIZATION: MARINE BIOGEOCHEMICAL PROVINCES AND DOCUMENTED RESPONSES

BIOGEOCHEMICAL PROVINCES

Phytoplankton have an absolute Fe requirement resulting from the non-substitutable role of this metal as an electron transporter in photosynthesis and respiration (Raven et al., 1999; Morel et al., 2003). Deep waters upwelling in the high latitude North Pacific, Equatorial Pacific, and the Southern Ocean have lower dissolved Fe:nitrate ratios than those required by phytoplankton (e.g., Johnson et al., 1997; Parekh et al., 2005; Sunda, 2012; Twining and Baines, 2013). Consequently, with the onset of favorable conditions for accumulation of plankton biomass (e.g., Sverdrup, 1953; Platt et al., 1991; Behrenfeld, 2010; Taylor and Ferrari, 2011), dissolved Fe can decline to concentrations that

restrict phytoplankton growth rates and standing stocks whilst nitrate remains available (**Figure 1**; Boyd et al., 2007; Moore et al., 2013). Strictly, both “high-nitrate low-chlorophyll” (HNLC) and “high-nitrate high-chlorophyll” (HNHC) conditions appear to occur in ocean regions where phytoplankton communities are experiencing Fe stress (e.g., Moore et al., 2007 found Fe-limited Southern Ocean phytoplankton at chlorophyll-a concentrations of 1.42 mg m^{-3} ; cf. global mean $\sim 0.3 \text{ mg m}^{-3}$). Thus, our use of “HNLC” throughout this manuscript will simply refer generically to regimes where full utilization of available nitrate through phytoplankton growth is prevented for some reason (Cullen, 1991).

Leaching experiments conducted on volcanic ash have shown low macronutrient:micronutrient release ratios relative to the stoichiometric requirements of phytoplankton (Frogner et al., 2001; Stefánsdóttir and Gislason, 2005; Duggen et al., 2007; Jones and Gislason, 2008; Lin et al., 2011; Olgun et al., 2013a,b). Whilst volcanic ash likely provides a limited supply of macronutrients to LNLC regions, these vast oligotrophic systems also represent a major niche for nitrogen fixing bacteria, which have additional Fe requirements due to the presence of this element within the required nitrogenase enzyme (Berman-Frank et al., 2001). Thus, Fe supply is anticipated to up regulate nitrogen fixation, thereby increasing the total fixed nitrogen inventory available to the phytoplankton community (Falkowski, 1997; Moore et al., 2009). However, in terms of phytoplankton biomass changes, responses to conventional dust deposition in these types of system have been highly variable (DiTullio and Laws, 1991; Young et al., 1991; Johnson et al., 2003; Westberry et al., 2005; Bonnet et al., 2008; Mackie et al., 2008; Moore et al., 2009; Schlosser et al., 2014), therefore phytoplankton responses to ash deposition should be anticipated to be similarly complex.

SHIPBOARD BIOASSAY EXPERIMENTS

A synthesis of phytoplankton responses to ash supply is provided in **Table 1**. Arguably the most convincing evidence that natural phytoplankton communities can access Fe supplied from volcanic ash has come from shipboard bioassay experiments that have detected changes in phytoplankton physiology (Achterberg et al., 2013; Browning et al., 2014a), biomass (Achterberg et al., 2013; Browning et al., 2014a; Mélançon et al., 2014), and community structure (Mélançon et al., 2014) that are consistent with relief of phytoplankton Fe limitation (Boyd et al., 2007). However, observed responses have not been consistent in either the magnitude of phytoplankton response to a given ash loading, or the relative response compared to parallel Fe-only treatment experiments. In the high latitude North Atlantic using fresh ash collected from the Eyjafjallajökull eruption <3 months previously, Achterberg et al. (2013) found a positive phytoplankton community-level response to ash supply, yet this was around half the magnitude of a 2 nmol L^{-1} Fe-only treatment. This was despite deionized water (Milli-Q) leaching experiments with the Eyjafjallajökull ash indicating an upper bound Fe release of $4.6\text{--}16 \text{ nmol L}^{-1}$. Conversely, Mélançon et al. (2014) observed changes in chlorophyll-a biomass in the North Pacific that generally matched Fe-only treatment—indicating full relief of Fe stress

in both cases, and Browning et al. (2014a) who in the Southern Ocean reported responses to ash amendment that were equivalent, or in a number of cases significantly enhanced relative to the Fe-only treatment.

The inconsistency between experiments across the three oceanic regions tested, despite similar ash loadings, is strongly suggestive of the importance of the biogeochemical regime and physiological state of the extant phytoplankton population being tested in controlling observed responses—as might be anticipated in any nutrient treatment experiment. This includes variability in the solubility and/or accessibility of the volcanic Fe under the particular physical and chemical characteristics of the seawater in question and its interaction with a given ash sample. For example, the reduced response to ash observed by Achterberg et al. (2013) may reflect either that the ash-released Fe was not as accessible to the phytoplankton community as that from the Fe-only treatment (in this case in the form of FeCl_3), or that the magnitude of Fe supply was simply lower, with experiments leaching significant Fe from the ash into Milli-Q water ($\text{pH} < 7$) potentially overestimating that which actually occurred within the seawater experiments. In contrast, Browning et al. (2014a), found full relief of Fe stress by ash treatment in Southern Ocean waters with lowest dissolved Fe concentrations (**Figures 2A,C**), and suggested that the significant experimental responses to ash compared to that with Fe-only treatment in several instances may point to relief of trace metal (co)limitation (perhaps manganese (Mn)) (see **Figure 2D**).

As well as supplying essential trace elements, volcanic ash releases metals that can be toxic to phytoplankton at high concentrations (Morel et al., 2003; Hoffmann et al., 2012). However, the results from the shipboard bioassay experiments suggest that, at least at ash loadings used in experiments so far that were chosen to represent realistic ash supply to the open ocean, there is an absence of toxicity at the community level. This is demonstrated by the similar or greater stimulation of phytoplankton compared with Fe-only treatment in the cases of Mélançon et al. (2014) and Browning et al. (2014a), or in the case of Achterberg et al. (2013), a similar level of response between Fe-only and Fe plus ash treatment.

LARGE SCALE BIOGEOCHEMICAL RESPONSES TO ASH DEPOSITION EVENTS

Whilst the bottle-scale experiments have been essential tools for direct monitoring of the phytoplankton response to ash supply, observations during and subsequent to large-scale natural ash deposition events have provided further insight into the extent of the biogeochemical response of the system in question. Specifically, anomalously low post-bloom nitrate concentrations within the Icelandic Basin provided good evidence for enhanced phytoplankton growth subsequent to the 2010 Eyjafjallajökull ash deposition event (Achterberg et al., 2013) in a region where an annual phytoplankton bloom (e.g., Siegel et al., 2002) has been reported to be terminated by insufficient Fe (Ryan-Keogh et al., 2013). Enhanced satellite-detected chlorophyll-a concentrations were also observed, however Henson et al. (2013) concluded that anomalously reduced mixed layer depths provided more favorable irradiance conditions for phytoplankton in the same season as the

Table 1 | Synthesis of previously reported phytoplankton responses to volcanic ash supply.

References	Study type	Ash type(s)	Ash concentration in seawater	Phytoplankton response to ash	Phytoplankton response to Fe only	Additional details
Watson, 1997	Atmospheric gas anomalies	Dacite (Phatubo 1991 eruption)	Unknown	Circumstantial evidence from atmospheric gas measurements	Not tested	Large scale Fe-fertilization hypothesized on the basis of hemispheric gradients in O ₂ /N ₂ . Also see Sarmiento (1993)
Uematsu et al., 2004	Remote sensing (SeaWiFS), <i>in-situ</i> gas and aerosol sampling	Basaltic, included ammonium sulfate particles (Miyake-jima 2000 eruption)	Unknown	Small month-averaged chlorophyll- <i>a</i> concentration increases (0.01–0.02 mg m ⁻³) inferred from SeaWiFS	Not tested	Suggested ammonium sulfate supply relieved phytoplankton of fixed nitrogen limitation
Duggen et al., 2007	Ash amendment of Fe-starved phytoplankton culture (diatom <i>Chaetoceros dichroaeta</i>)	Subduction zone volcanic ash (specific type/source not reported)	Unknown—see additional details	Significant stimulatory F_v/F_m^a and chlorophyll- <i>a</i> response to ash amendment over 18 days	Not tested	Fe-starved phytoplankton culture exposed to ash for 15–20 min
Langmann et al., 2010a	Remote sensing (MODIS)	Kasatochi 2008 eruption: basaltic-andesitic	Uncertain—see additional details	Approximate doubling of MODIS-detected chlorophyll- <i>a</i> concentration in August 2008 relative to climatological averages over an area of anticipated ash deposition	Not tested	Langmann et al. (2010a) estimated Kasatochi 2008 ash deposition at 4.5–6 × 10 ¹¹ kg into the NE Pacific based on magnitude of satellite-detected phytoplankton bloom. Equivalent to ~10 mg L ⁻¹ Mélançon et al., 2014
Hamme et al., 2010	Remote sensing (SeaWiFS and MODIS); autonomous sensors at OSP ^b ; cruise-based analysis of primary production and phytoplankton pigment samples	Kasatochi 2008 eruption: basaltic-andesitic	Unknown (although see Langmann et al., 2010a)	Approximate doubling of SeaWiFS and MODIS-derived August 2008 chlorophyll- <i>a</i> concentrations in an area of anticipated ash deposition over any month between 1997 and 2010. Increased mixed-layer fluorescence and reduced pCO ₂ at OSP ^b	Not tested	Research cruise in the region also measured increased chlorophyll- <i>a</i> concentrations and shift to diatom dominated community. Shipboard estimates of gross primary production double that of previous year
Lin et al., 2011	Remote sensing (MODIS)	Anatahan 2003: andesitic-dacitic	Unknown, although estimated in the current study as ~50 g ash m ⁻³ (50 mg L ⁻¹)	MODIS-derived chlorophyll- <i>a</i> increase 8–16 times that of surrounding waters; fluorescence line height increases of 2–5 times	Not tested	Shift in spectra of remote sensing reflectance indicating increased contribution of the nitrogen fixing species <i>Trichodesmium</i> to the extant community

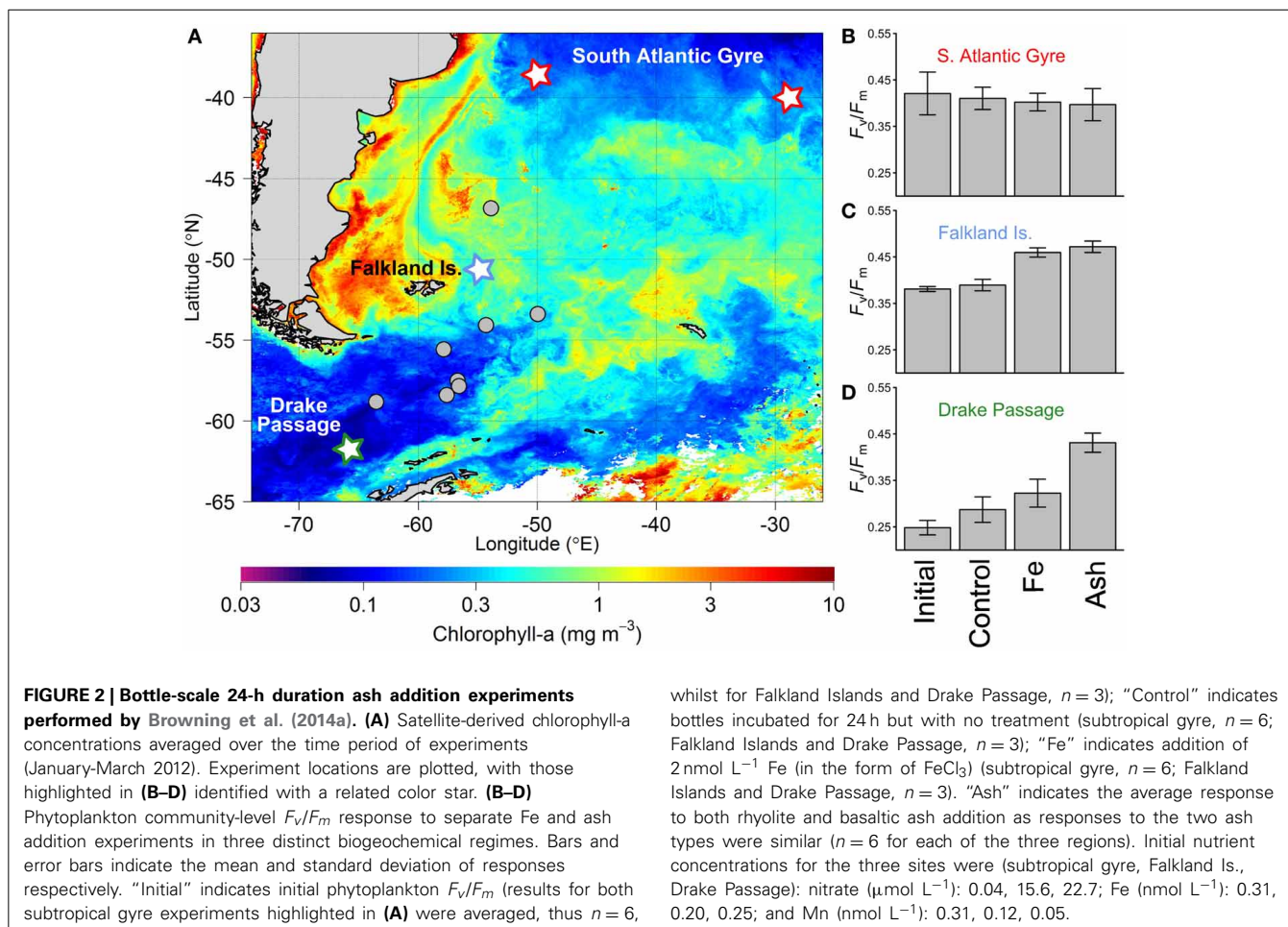
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Table 1 | Continued

References	Study type	Ash type(s)	Ash concentration in seawater	Phytoplankton response to ash	Phytoplankton response to Fe only	Additional details
Hoffmann et al., 2012	Growth rates of phytoplankton cultures using growth media previously treated with ash	Arenal 1993: andesite; Popocatepetl 2000: andesite; Rabaul-Tavurvur 2002: andesite-basalt; Sakura-jima 2007: andesite-dacite; Apoyeque 1.9 ka: dacite	0.53, 1.07, 1.6, and 2.67 g ash L ⁻¹ (equivalent concentrations—see additional details)	Diatom <i>Thalassiosira pseudonana</i> showed generally elevated growth rates; Coccolithophore <i>Emiliania huxleyi</i> showed decreased growth rate with media exposed to Sakura-jima ash and little response to other ash types	Not tested	Ash added to a seawater solvent, before filtration and dilution of the solute to generate culture growth media
Achterberg et al., 2013	1 × 5 day shipboard bioassay experiment in the high latitude N. Atlantic; Direct under plume and post-eruption biological and chemical analysis; Remote sensing (MODIS) chlorophyll- <i>a</i> concentration analysis	Ash from the Eyjafjalajökull 2010 eruption: basaltic-andesitic	9 mg ash L ⁻¹ used in bioassay experiment	Significant stimulatory F_v/F_m^a (24 h) and chlorophyll- <i>a</i> (72 h) response to ash amendment in bottle experiment. Early occurrence of spring-summer phytoplankton bloom detected by remote sensing (MODIS) chlorophyll- <i>a</i> concentrations. Increased bloom magnitude indicated by enhanced nitrate drawdown in high latitude North Atlantic	Response to 2 nmol Fe L ⁻¹ (FeCl ₃ form) treatment was around double that of ash treatment	Treatment with volcanic ash plus Fe produced similar response to Fe only, indicating an absence of significant ash toxicity at the community level. Evidence for large scale fertilization from Eyjafjalajökull 2010 eruption remains circumstantial (see Henson et al., 2013)
Mélançon et al., 2014	1 × 6 day shipboard bioassay experiment in the high latitude N. Pacific (site close to OSP ^b)	Kasatochi 2008: basalt-andesite; Chaitén 2008: rhyolite	Kasatochi ash: 1.2 mg ash L ⁻¹ Chaitén ash: 0.12, 1.2, and 10 mg ash L ⁻¹	Doubling in chlorophyll- <i>a</i> after 6 days incubation for all ash treatments except 0.12 mg Chaitén ash L ⁻¹	Similar level of phytoplankton response to ash treatments as for treatment with 0.6 nmol Fe L ⁻¹ (FeSO ₄ form)	Phytoplankton responses also included increased carbon uptake (¹³ C-uptake measurements) and net phytoplankton growth rate (via 4–6 day chlorophyll- <i>a</i> changes), alongside a community structure shift toward increased diatom contribution
Browning et al., 2014a	21 × 24–48 h shipboard bioassay experiments in the South Atlantic and Southern Ocean	Chaitén 2008: rhyolite Etna 2002: basalt	0.1 mg ash L ⁻¹ to 250 mg ash L ⁻¹	No response to ash detected in South Atlantic subtropical gyre. Variable responses in Southern Ocean, including significant stimulatory F_v/F_m^a (24 h) and chlorophyll- <i>a</i> (48 h) responses	Where any response to Fe-only treatment (2 nmol Fe L ⁻¹) in the Southern Ocean was detected, response always equivalent or greater in parallel ash-amended bottles	Enhanced response of Southern Ocean phytoplankton communities to ash suggested to be a result of relief of community Mn (co)limitation (see Figure 2)

^a F_v/F_m , physiological parameter used as a proxy for Fe stress status (Behrenfeld and Milligan, 2013).

^b OSP Ocean Station Papa (see **Figure 1** for location).



ash deposition event, complicating attribution of the enhanced phytoplankton bloom in this year.

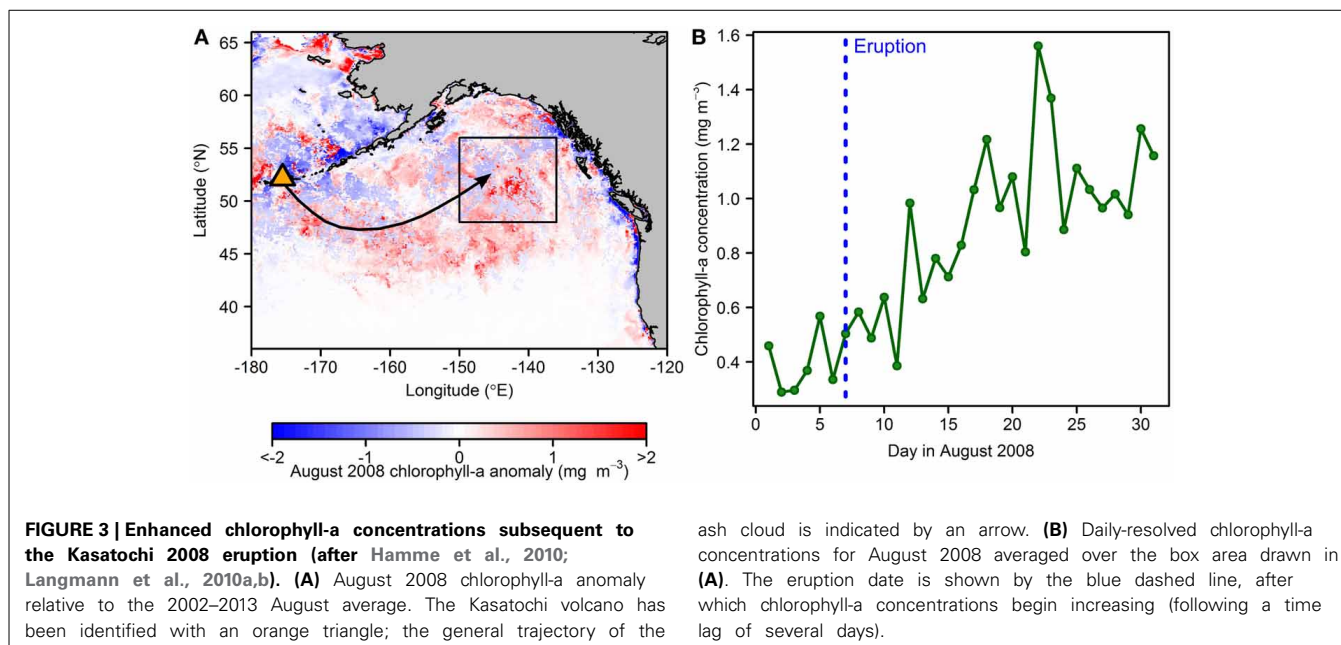
More convincing evidence of large-scale ash fertilization has come from multiple observations of the Kasatochi 2008 deposition event in the high latitude North Pacific (Hamme et al., 2010; Langmann et al., 2010a). Satellite-derived chlorophyll-a concentrations averaged for August 2008 over an area downwind (east) of the eruption and within a region shown to be Fe-stressed at this time of year (Tsuda et al., 2003; Boyd et al., 2004) were double that of any monthly average since 1997 (Hamme et al., 2010; Figure 3A). Critically, ground-based measurements strongly supported the occurrence of enhanced phytoplankton growth after the ash deposition event. Ash was entrained in a storm system, and deposited over a wide areal extent, including the Ocean Station Papa (OSP) site where a sea glider detected enhanced chlorophyll-a fluorescence and a pCO_2 (CO_2 partial pressure) instrument at Station P monitored clear reductions suggesting enhanced phytoplankton growth (Hamme et al., 2010). These measurements were supported by cruise-based observations of enhanced chlorophyll-a and a phytoplankton community structure shift toward an increased contribution of diatoms. Later studies have suggested that this diatom bloom fueled higher trophic levels in the Gulf of Alaska: specifically zooplankton in 2008 (Hamme et al., 2010) and sockeye

salmon in 2010 (Parsons and Whitney, 2012; Olgun et al., 2013b).

There have been few investigations of phytoplankton responses to ash supply in LNLC regions, both in terms of shipboard bioassay experiments and larger scale biogeochemical responses subsequent to natural events. Browning et al. (2014a) performed ash amendment experiments in the South Atlantic subtropical gyre, yet observed no response in the 24-h duration experiments. It remains possible that some level of response may have been observed in longer duration experiments, where the stimulation of initially rare nitrogen fixing cyanobacteria increases the fixed nitrogen inventory for the extant phytoplankton community. Indeed, Lin et al. (2011) reported apparent chlorophyll-a concentrations to increase to 8–16 times that of surrounding LNLC oligotrophic waters subsequent to the 2003 Anatahan eruption, alongside a spectral shift in satellite-retrieved radiances consistent with a change in community composition toward an increased contribution of the nitrogen fixing species *Trichodesmium*.

OBSERVING BIOGEOCHEMICAL RESPONSES TO ASH DEPOSITION: CHLOROPHYLL-A REMOTE SENSING AND CONSTRAINING UNCERTAINTY IN CARBON EXPORT

Remote sensing provides both invaluable quasi-synoptic coverage of ocean color (and thus a means to estimate chlorophyll-a



concentrations) and atmospheric aerosol loading; however, as acknowledged in studies focusing on conventional dust-fueled fertilization events (Boyd et al., 2010), linking the two causatively without field observations is potentially complicated by a range of factors. Spatial coverage of satellite-retrieved ocean color for a given day or composited over a weekly timescale can be far from complete, whilst compositing over longer time periods could hide spatial and temporal patterns between a given ash deposition event and phytoplankton response. Furthermore, phytoplankton responses in the ocean will rarely be as simple as observed in a bottle experiment (Cullen et al., 1992), with a multitude of complex and interacting physical (e.g., Lewis et al., 1984; Platt et al., 1991; Abraham, 1998; Abraham et al., 2000) and ecological (e.g., Banse, 1992; Landry et al., 2000; Behrenfeld, 2010; Behrenfeld et al., 2013) factors, in addition to nutrient availability, regulating the standing stock of phytoplankton at any given point and time. These factors are not easily recovered by remote sensing, typically requiring a suite of detailed measurements at sea to resolve (e.g., Boyd et al., 2007; Landry et al., 2009). Additionally, chlorophyll-a concentrations are not a direct measure of phytoplankton biomass (e.g., Strickland, 1960; Cullen, 1982), as pigment:carbon ratios are strongly dependent on growth conditions (e.g., Geider, 1987). Finally, loading of surface waters with volcanic ash may alter optical properties of seawater such that chlorophyll-a concentrations estimated using conventional ocean-color sensors and algorithms would be ambiguous.

Despite the array of aforementioned difficulties, the often remote and sporadic nature of ash deposition events mean that detection via satellite is typically the only method of observation available; justifying the current effort to constrain potential for monitoring ash-mediated fertilization in this manner. Moreover the point-source and often transient nature of volcanic eruptions alongside their coincident diagnostic gas emission should make ash deposition events more easily traceable via remote sensing

than regular desert dust. In the following section we conduct a study to (i) evaluate the potential impact of suspended ash on chlorophyll-a concentrations estimated by conventional Case 1 ocean-color algorithms, and (ii) perform a retrospective analysis of events depositing ash into ocean waters spanning a range of biogeochemical settings. We finish by evaluating the potential role of ash fertilization on carbon export using current estimates of nutrient release from volcanic ash and carbon export efficiencies.

MATERIALS AND METHODS

Determining the inherent optical properties of rhyolitic ash suspended in seawater

Inherent optical properties relevant for satellite ocean color remote sensing were assessed for Chaitén ash samples suspended in filtered seawater (0.2/0.2 μm Pall Acropak1000® Capsule) using a flow through system in-line with optical sensors (Dall’Olmo et al., 2009). The Chaitén ash used was sample 05-15b of Watt et al. (2009) from the May 2008 eruption, as used in the bottle-scale fertilization experiments of Browning et al. (2014a). The ash sample had a modal grain size of 62.5 μm and was almost exclusively a rhyolitic glass (bulk density of individual particles of rhyolite glass $\sim 2400 \text{ kg m}^{-3}$; some particles in the $>100 \mu\text{m}$ fraction are vesicular so bulk particle densities of these individual particles will be lower) (Watt et al., 2009). Details of the 2008 source eruption, ash collection, and bulk chemical analyses are described in Watt et al. (2009). Optical backscattering coefficients ($b_b(\lambda)$) were measured at three wavelengths (470, 532, and 700 nm) using an ECO-BB3 backscattering meter (WET Labs). Absorption coefficients ($a(\lambda)$) were measured at nine wavelengths (412, 440, 488, 510, 532, 555, 650, 676, and 715 nm) over a 25 cm path length using an ac-9 spectral absorption-attenuation meter (WET Labs) (Dall’Olmo et al., 2009). Each experimental session started with cleaning the system

(4.06 L volume) with Decon 90 and a weak solution of bleach that was rinsed and drained before refilling with filtered seawater. A known amount of ash mass was then added directly to the system at progressively increasing concentrations (see **Table 1** for ash concentrations). Water with the new sample addition was circulated through the system using a peristaltic pump (Watson Marlow) at 4 L min⁻¹ for at least 3 min or until readings were stable. Following this the pump was switched off and real-time observations of backscattering and absorption were recorded for 3 min (fluctuations within this time were less than 5% of the signal magnitude).

As has been found previously for measurement of pure quartz particle suspensions (e.g., Babin and Stramski, 2004; Stramski et al., 2007) absorption coefficients for the Chaitén ash were below the detectable level of the instrument across the entire spectrum (limit of detection for the ac-9 reported as 3 × standard deviation of blanks is ~0.009 m⁻¹; Twardowski et al., 1999). For this reason we assumed a spectrally-insensitive value of 0.0001 m² g⁻¹ that is consistent with the lowest values reported in the modeling study of Wozniak and Stramski (2004). Particulate backscattering coefficients at a given concentration ($b_{bp,raw}$) were derived as recommended by the manufacturer using modifications for chamber measurements (Dall’Omo et al., 2009):

$$b_{bp,raw} = 2\pi \chi_p (\beta - \beta_{SW}) - b_{b,wall}, \quad (1)$$

where χ_p is conversion factor (1.076, Sullivan et al., 2013), β is the volume scattering function at the measurement angle of the backscattering meter (124°), and $b_{b,wall}$ is the backscattering coefficient associated with the flow-through tube. The pure water volume scattering function (β_{SW}) from Zhang et al. (2009) ($T = 21.3$ °C, $S = 35.1$ psu) was subtracted from β . Values of $b_{bp,raw}$ were then converted to an ash-only backscattering ($b_{bp,ash}$) by subtracting the $b_{bp,raw}$ of the filtered seawater case from the ash-loaded case in order to remove any potential background contamination in the system. Mass-specific ash backscattering ($b_{bp,ash}^*$) were calculated by dividing $b_{bp,ash}$ by the ash concentration.

We followed the approach of Wozniak and Stramski (2004) to estimate the relative contribution of suspended ash to chlorophyll concentrations retrieved by ocean color sensors and Case 1 algorithms. Firstly the remote sensing reflectance values ($R_{rs}(\lambda)$), from which satellite-based chlorophyll-a concentrations are derived, were assumed to vary as the ratio of the total seawater backscattering to the sum of the total seawater backscattering and absorption coefficients:

$$R_{rs}(\lambda) \propto \frac{b_b(\lambda)}{b_b(\lambda) + a(\lambda)}, \quad (2)$$

where b_b is total backscattering coefficient of seawater and a is total absorption coefficient of seawater. The total backscattering and absorption of seawater includes the individual components of phytoplankton, ash and the seawater itself:

$$a(\lambda) = a_w(\lambda) + a_{ash}^*(\lambda) C + a_p(\lambda), \quad (3)$$

$$b_b(\lambda) = b_{b,w}(\lambda) + b_{bp,ash}^*(\lambda) C + b_{b,p}(\lambda), \quad (4)$$

where a_w is absorption of pure seawater, a_{ash}^* is the mass-specific absorption of ash particles, C is ash particle concentration, and a_p is absorption of phytoplankton (and equivalent for backscattering). Absorption and backscattering for pure seawater and phytoplankton were parameterized as for Wozniak and Stramski (2004) (and references therein). Backscattering coefficients for the Chaitén ash at the wavelengths used by ocean color sensors were estimated from the values in **Table 2** and the following power law (Snyder et al., 2008):

$$b_{bp,ash}^*(\lambda) = b_{bp,ash}^*(532) \left(\frac{\lambda}{532} \right)^{-\eta}, \quad (5)$$

Where η was determined from an ordinary least squares regression on the log-transformed values of $b_{b,ash}^*$ and λ . Chlorophyll-a concentrations estimated from ocean color typically use Case 1 algorithms that employ the ratio of retrieved remote sensing reflectance in the blue and green regions of the spectrum (R_r) alongside an empirically derived relationship with chlorophyll-a:

$$R_r = \log \left(\frac{R_{rs}(blue)}{R_{rs}(green)} \right) \quad (6)$$

$$Chlorophyll-a = 10^{(a_0 + a_1 R_r + a_2 R_r^2 + a_3 R_r^3 + a_4 R_r^4)} \quad (7)$$

Where blue and green represent chosen wavelengths that differ for the various ocean color sensors and associated algorithms. We used the OC3M-547 algorithm that is used by the NASA ocean color processing group to generate the MODIS chlorophyll-a images in this paper (see: <http://oceancolor.gsfc.nasa.gov/REPROCESSING/R2009/ocv6/>). For this algorithm $R_{rs}(blue)$ is the larger of either $R_{rs}(443)$ or $R_{rs}(489)$ and $R_{rs}(green)$ is $R_{rs}(547)$ and the empirically derived parameters are: $a_0 = 0.02424$; $a_1 = -2.7423$; $a_2 = 1.8017$; $a_3 = -0.0015$; $a_4 = -1.2280$.

Table 2 | Inherent optical properties of Chaitén ash^a.

Ash concentration (g m ⁻³)	$b_{b,ash}^*(\lambda)$ [m ² g ⁻¹]		
	470	532	700
10.8	0.00019	0.00014	0.00007
16.6	0.00017	0.00012	0.00006
26.7	0.00020	0.00013	0.00008
35.1	0.00014	0.00010	0.00007
50.4	0.00016	0.00011	0.00007
Median $b_{b,ash}^*(\lambda)$ [m ² g ⁻¹]	0.00017	0.00012	0.00007
SD $b_{b,ash}^*(\lambda)$ [m ² g ⁻¹]	2.23E-05	1.65E-05	7.33E-06

^a $b_{b,m}^*$ is the mass specific backscattering of suspended ash for the 5 loading experiments; SD = standard deviation. The median percentage uncertainties of $b_{b,wall}$ on $b_{bp,raw}$ (see Section: “Determining the Inherent Optical Properties of Rhyolitic Ash Suspended in Seawater”) for the suite of ash concentrations were 9%, 8% and 14% respectively for the three backscattering channels (470, 532, and 700 nm).

Determining the impact of suspended ash on light availability for phytoplankton

Using the inherent optical properties described previously (Section: “Determining the Inherent Optical Properties of Rhyolitic Ash Suspended in Seawater”), a simple calculation was performed to evaluate the impact of suspended Chaitén ash on light availability for phytoplankton. The vertical attenuation coefficient for downward irradiance at the mid-point of the photic zone ($K_d(z_m, \lambda)$) was calculated using the equation presented by Kirk (1981):

$$K_d(z_m, \lambda) = [a(\lambda)^2 + 0.256a(\lambda)b_b(\lambda)]^{0.5}, \quad (8)$$

where $a(\lambda)$ and $b_b(\lambda)$ are total seawater absorption and backscattering at a given wavelength, λ (see Equations 3–4), and z_m is the mid-point of the euphotic zone. $K_d(z_m, \lambda)$ at $\lambda = 443$ nm calculated for waters containing suspended ash was divided by the case with no ash to give the relative influence of ash on light attenuation at this wavelength. Making the assumption of a constant K_d throughout the photic zone, this quotient is equivalent to the factor that the euphotic depth (i.e., depth at which light is 1% of its surface value) would be reduced by.

Remote sensing data

All chlorophyll-a products used in this study are 4-km resolution L3 MODIS composites either at 1-day, 8-day or monthly averaged formats available from NASA (see: <http://oceancolor.gsfc.nasa.gov/>). These products have been generated using the OC3M-547 algorithm developed for open ocean Case 1 waters. Case 1 waters are those in which phytoplankton and co-varying biological material are predominantly responsible for controlling the inherent optical properties of the water (Gordon and Morel, 1983). Alongside the presence of any other non-algal particles, suspended volcanic ash is not accounted for in the atmospheric correction for water-leaving radiances used in this algorithm, with the magnitude and sign of any resultant bias unknown. Using new optical measurements we present the first quantitative analysis of the potential impact of suspended volcanic ash on retrieved chlorophyll-a to assess for bias in each of the presented case studies (see Section: “Determining the Inherent Optical Properties of Rhyolitic Ash Suspended in Seawater”).

Various approaches have been employed for observing the spatial extent and loading of ash plumes; in this study we used UV aerosol index products from: (i) the Total Ozone Mapping Spectrometer (TOMS) on the Nimbus-7 satellite for data from 1978 to 1993 (e.g., Seftor et al., 1997) and, (ii) the Ozone Monitoring Instrument (OMI) on the EOS-Aura satellite for data from 2004-present (e.g., Torres et al., 2007). Products from both missions are available from NASA (<http://ozoneaq.gsfc.nasa.gov/>).

To aid with interpretation of chlorophyll-a changes as a function of ash loading, satellite products for other key physical variables potentially regulating phytoplankton dynamics were downloaded: MODIS sea surface temperature at the same temporal and spatial resolutions as chlorophyll-a; fields of multi-sensor blended wind stress from the NOAA National Climatic Data Center (<http://ncdc.noaa.gov/>); and images of sea surface

height from the Colorado Center for Astrodynamic Research (http://eddy.colorado.edu/ccar/ssh/hist_global_grid_viewer).

Ash deposition events investigated (Table 3) were targeted as those sourced from eruptions with larger explosivity and eruption volumes (Volcanic Explosivity Index, VEI > 3) and with a greater chance of deposition over the ocean. Chlorophyll-a responses were evaluated as post-ash deposition concentration changes around a pre-eruption baseline over a spatial region of anticipated ash deposition inferred from the aerosol products (see Figure 4 caption for further details).

Calculations of potential bounds for ash-fertilized carbon export

Assuming known masses of ash deposition and, guided by published estimates, prescribing continuous vectors of Fe release efficiency (Fe release per unit mass of ash) and carbon export efficiency (carbon sequestration per unit mass of Fe addition), matrices of potential carbon export were calculated for 3 events varying by two orders of magnitude by mass of oceanic ash deposition.

A crude estimate of ash deposition was calculated for the past 16.5 kyr for the volcanoes of present-day southern Chile and Patagonia (Llaima to Hudson—see Figure 1; Watt et al., 2013; Fontijn et al., 2014). In this arc segment, 87 explosive eruptions from 24 volcanoes are known to have had eruptions with a VEI of at least 4, with a minimum eruptive yield of 132 km³ of tephra in 16.5 kyr (Watt et al., 2013). Each of these eruptions would have delivered substantial volumes of ash to the Southern Ocean, both during eruptions, and through later wind-borne remobilization. Studies of the Hudson 1991 and Chaitén 2008 eruptions have suggested that at least 30–40% of the erupted ash volume in each case was deposited as primary ash fallout to the South Atlantic-Southern Ocean (Scasso et al., 1994; Watt et al., 2009). This proportion is conservative—and will be higher for larger eruptions as the dispersal area increases. Assuming 35%, and a (conservative) ash bulk density of 1 ton m⁻³ produces an ash mass flux of ~50 Pg. Whilst the bulk Fe content of rhyolitic ash can reach >4% (e.g., Watt et al., 2009), recent experiments (e.g., Duggen et al., 2007; Jones and Gislason, 2008; Olgun et al., 2011; Achterberg et al., 2013; Browning et al., 2014a; Mélançon et al., 2014) suggest that the majority of this Fe does not become part of the dissolved pool on the timescale the ash sinks through the water column (<1–2 days; Duggen et al., 2007). Therefore, we refined the assumption made in the earlier calculation of Watson (1997), who estimated 1% by weight of deposited Pinatubo ash to be bioavailable Fe, by assuming an Fe release range of 1 × 10⁻⁶ to 1 × 10⁻⁵ g Fe (g ash)⁻¹ (equivalent to a solubility of 0.025–0.0025% for a 4 wt% Fe content of ash; after Gaiero et al., 2003; Watt et al., 2009). The lower end of this range reflects the results of Browning et al. (2014a) (~1 × 10⁻⁶ g Fe (g ash)⁻¹) and Mélançon et al. (2014) (~1.7 × 10⁻⁶ g Fe: (g ash)⁻¹, inferred from the reported ~0.1–0.5 nmol L⁻¹ dissolved Fe increase in seawater subsequent to addition of 10 mg ash L⁻¹), whilst the upper range reflects the ~0.2 μmol Fe (g ash)⁻¹ found by Olgun et al. (2011). With these assumptions Patagonian total 16.5 ka to present-day volcanic Fe supply was calculated as 50–500 Gg Fe.

Calculated ranges of Fe release were used alongside a potential range of carbon export efficiency. Considerable uncertainty also

Table 3 | Summary of remote sensing case studies discussed in order of occurrence (1999–2014)^a.

Volcano name	Region	Regime	Eruption start date	Max. VEI	Ash type	Sat. chl-a increase detected?	Comment	References
Shiveluch	N. Pacific	HNLC	Aug 15th 1999	4	Andesitic	No	Onshore winds—limited ash dispersion over ocean	This study
Miyake-jima	W. St. Pacific	LNLC	Jun 27th 2000	3	Basaltic	Yes*	Fertilization through supply of ammonium sulfate?	Uematsu et al., 2004
Ulawun	W. Pacific (equatorial)	LNLC	Sep 28th 2000	4	Basaltic-andesitic	No*	Wind direction favorable for oceanic ash deposition	This study
Ruang	W. Pacific (equatorial)	LNLC	Sep 25th 2002	4	Basaltic-andesitic	No	Onshore winds—limited ash dispersion over ocean	This study
Reventador	E. Pacific (equatorial)	HNLC	Nov 3rd 2002	4	Andesitic	No	Poor satellite coverage	This study
Anatahan	W. Pacific (subtropical)	LNLC	May 10th 2003	3	Andesitic-dacitic	Yes*	Chlorophyll-a increase and remote sensing of <i>Trichodesmium</i>	Lin et al., 2011
Manam	W. Pacific (equatorial)	LNLC	Oct 24th 2004	4	Basaltic-andesitic	No	Onshore winds—limited ash dispersion over ocean	This study
Sierra Negra	E. Pacific (equatorial)	HNLC	Oct 22nd 2005	3	Basaltic	No		This study
La Cumbre	E. Pacific (equatorial)	HNLC	May 13th 2005	2	Basaltic	No		This study
Rabaul	W. Pacific (equatorial)	LNLC	Aug 11th 2006	4	Andesitic-dacitic	No	Onshore winds—limited ash dispersion over ocean	This study
Llaima	S. Atlantic	HNLC	Jan 1st 2008	3	Basaltic-andesitic	No	Limited ash deposition?	This study
Chaitén	S. Atlantic	HNLC	May 2nd 2008	4	Rhyolitic	Yes	Anomalously high chlorophyll-a in Malvinas-Brazil confluence	This study
Kasatochi	N. Pacific	HNLC	Aug 7th 2008	4	Basaltic-andesitic	Yes	Supporting ancillary measurements from OSP/routine OSP cruises	Hamme et al., 2010; Langmann et al., 2010a
La Cumbre	E. Pacific (equatorial)	HNLC	Apr 10th 2009	2	Basaltic	Yes	Chlorophyll-a increase in time series but uncertain if ash causative	This study
Sarychev Peak	N. Pacific	HNLC	Jun 11th 2009	4	Basaltic-andesitic	No	Poor satellite coverage	This study
Eyjafjallajökull	N. Atlantic	HNLC	Mar 20th 2010	4	Basaltic-andesitic	Yes	Chlorophyll-a anomaly but uncertain if ash causative	Achterberg et al., 2013; Henson et al., 2013
Merapi	E. Indian (equatorial)	LNLC	Oct 26th 2010	4	Andesitic	No	Poor satellite coverage	This study
Puyehue-Cordón Caulle	S. Atlantic/S. Ocean	HNLC	Jun 4th 2011	5	Rhyolitic	No	Poor satellite coverage; austral winter—phytoplankton light-limited?	This study
Kelud	E. Indian (equatorial)	LNLC	Feb 26th 2014	4	Basaltic-andesitic	No	Poor satellite coverage	This study

^a See **Figure 1** for geographic locations of volcanoes. VEI, Volcanic explosivity index; HNLC, high-nitrate, low-chlorophyll; LNLC, low-nitrate, low chlorophyll; OSP, Ocean Station Papa. "Poor satellite coverage" indicates that a high proportion of pixels in images of interest were masked, for example due to cloud cover, high sun glint, low winter irradiance etc. Satellite chlorophyll-a changes highlighted with a star are events with seaward ash deposition into waters with ocean color coverage that have low initial chlorophyll-a concentrations ($<0.1 \text{ mg m}^{-3}$); optical experiments on rhyolitic ash conducted in this study suggest significant resultant chlorophyll-a bias in such cases (see **Figure 4**). Eruption start dates, VEI's, and ash types are from <http://www.volcano.si.edu/>.

exists in this latter parameter (e.g., De Baar et al., 2005; Sarmiento et al., 2010; Boyd et al., 2012), yet what has become evident from recent deliberate Fe fertilization experiments and observations of natural Fe enrichments is that the amount of Fe addition required for a given mass of carbon export appears to be far greater (i.e.,

less carbon export per added Fe) than projected using typical stoichiometric requirements measured in phytoplankton [also assumed in the earlier calculation of Watson (1997)]. We use a range in carbon export efficiency of $1000\text{--}30,000 \text{ g C (g Fe)}^{-1}$ that encompasses the results of several Fe natural and anthropogenic

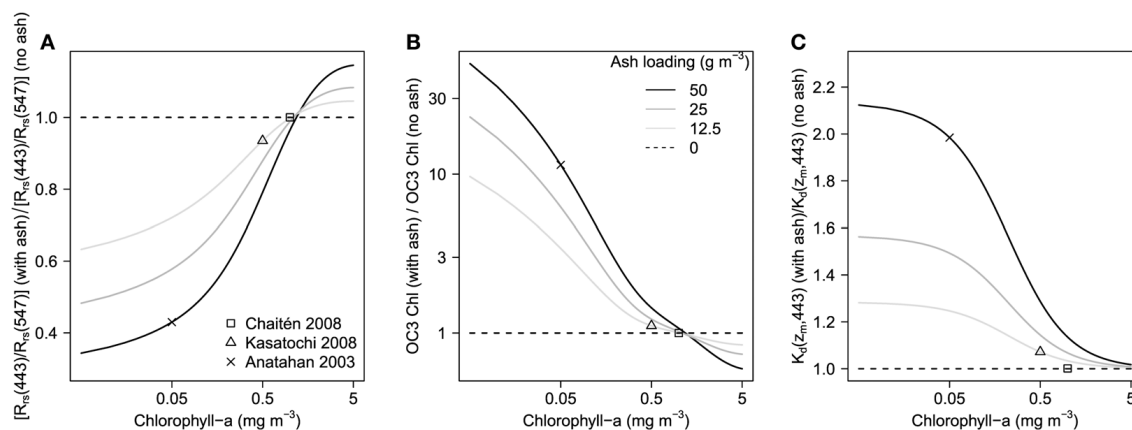


FIGURE 4 | Relative influence of suspended Chaitén ash on (A) the satellite-retrieved blue:green R_{rs} ratio, (B) resultant OC3-derived chlorophyll-a concentrations (using $R_r = R_{rs}(443)/R_{rs}(547)$), and (C) $K_d(z_m, \lambda)$. Ash-biased values are normalized to the no-ash case for three ash loadings at a range of seawater chlorophyll-a concentrations. The influences of the expected ash loading for three eruptions that have been investigated for phytoplankton response in this study are highlighted (note that apart from Chaitén 2008, the applicability of these optical properties to the other ash types are uncertain). “Actual” seawater chlorophyll-a has been estimated from the pre-eruption satellite-retrieved concentrations. The estimated ash loading has a variable sensitivity to the relative level of bias depending on the

seawater chlorophyll-a concentration (note the logarithmic scale on the vertical axis in B). For each of the highlighted case studies ash loading has been estimated as follows; Kasatochi 2008: 10 g m^{-3} , consistent with the mixed layer concentrations employed by Mélançon et al. (2014) who used the modeling estimates of Langmann et al. (2010a,b); Chaitén 2008: 0.5 g m^{-3} from the $9 \times 10^9 \text{ kg}$ ash ocean deposition estimated by Watt et al. (2009) over an area of $7 \times 10^{11} \text{ m}^2$ and a mixed layer of 30 m (de Boyer Montégut et al., 2004); Anatahan 2003: 50 g m^{-3} , from the $0.5 \times 10^{10} \text{ kg}$ of ash estimated by Lin et al. (2011) after Trusdell et al. (2005) over the area of apparent satellite detected chlorophyll-a response ($4.85 \times 10^9 \text{ m}^2$) and a 20 m mixed layer (Lin et al., 2011).

enrichment experiments, as summarized by Sarmiento et al. (2010).

Calculations were subsequently carried out in the same manner for the eruptions of Mounts Hudson and Pinatubo in 1991 and Kasatochi in 2008. Ocean-bound ash fluxes from Mounts Hudson and Pinatubo in 1991 of 3.25 and 0.004 Pg were calculated from values reported in Watson (1997) and Scasso et al. (1994) respectively, again for the Hudson eruption applying a conservative bulk ash density of 1 ton m^{-3} to the reported erupted volume. We assumed that the Fe release efficiency was similar to that for the Chaitén ash (1×10^{-6} to $1 \times 10^{-5} \text{ g Fe (g ash)}^{-1}$), producing an Fe flux range of 3.25–32.5 Gg Fe. The Kasatochi 2008 bulk ash flux was estimated at 0.6 Pg after Langmann et al. (2010a,b). Upper and lower Fe release efficiencies for ash from the 2008 Kasatochi eruption, reported by Olgun et al. (2013b), also fall within the same range proposed above for Chaitén ash (3.4×10^{-6} to $4.6 \times 10^{-6} \text{ g Fe (g ash)}^{-1}$). Thus, using the same range of Fe release efficiency produces a Kasatochi Fe flux range of 0.6–6 Gg Fe.

RESULTS AND DISCUSSION

INHERENT OPTICAL PROPERTIES OF CHAITÉN ASH SUSPENDED IN SEAWATER

Impact of Chaitén ash on satellite retrieved chlorophyll-a

Figures 4A,B shows how the $R_{rs}(\text{blue}) : R_{rs}(\text{green})$ ratio (here using $R_{rs}(443)/R_{rs}(547)$) and resultant OC3-derived chlorophyll-a concentrations are impacted by Chaitén ash loading, for three ash concentrations at a range of seawater chlorophyll-a. As has been demonstrated for other mineral particles (e.g. Wozniak and Stramski, 2004), seawater chlorophyll-a concentration is a

major factor regulating the relative impact of ash contamination. Chaitén ash is a “pure scatterer” (i.e., its absorption does not vary spectrally); thus the effect of ash addition always has a higher proportional effect on the lower magnitude R_{rs} . At low chlorophyll-a concentrations ($< 1.2 \text{ mg m}^{-3}$) the lower R_{rs} is in the green, thus $R_{rs}(\text{green})$ increases relatively more than $R_{rs}(\text{blue})$ subsequent to ash contamination. This has the effect of reducing $R_{rs}(\text{blue}) : R_{rs}(\text{green})$ and satellite-estimated chlorophyll-a concentrations are accordingly biased upwards. At high seawater chlorophyll-a concentrations ($> 1.2 \text{ mg m}^{-3}$) R_{rs} is lower in the blue (as phytoplankton absorb strongly at this wavelength), thus the relative increase in $R_{rs}(\text{blue})$ is greater than the relative increase in $R_{rs}(\text{green})$. This leads to higher $R_{rs}(\text{blue}) : R_{rs}(\text{green})$ ratio and biases chlorophyll-a concentrations downwards, with the relative magnitude of this bias being much less than for the low (i.e., $< 0.5 \text{ mg m}^{-3}$) seawater chlorophyll-a concentration scenario. There is a cross-over point at around $1.2 \text{ mg chlorophyll-a m}^{-3}$ where the presence of Chaitén ash exerts no bias on retrieved reflectance ratios and remote sensing estimates of chlorophyll-a. As described above we assumed a spectrally-flat $a_{ash}^*(\lambda)$ value of $0.0001 \text{ m}^2 \text{ g}^{-1}$; the effect of increasing (reducing) this is to steepen (flatten) the curves of Figure 4 such that bias is greater (lower) at any point apart from the x-intercept.

These calculations only use the inherent optical properties we have measured for Chaitén ash (to our knowledge there have been no such measurements on other volcanic ashes) and significant variability may be expected as the refractive index and particle size spectrum varies for other ash types (see Wozniak and Stramski, 2004). Moreover, even for the same type of ash, size spectra shifts would be expected with distance from source

as coarser particles fall out of the eruptive plume first. However, these initial results give us a first order indication of the potential impact of a given suspended ash concentration in biasing retrieved chlorophyll-a estimated by conventional Case 1 algorithms. Thus, for the case studies presented in Section: “Remote Sensing of Phytoplankton Response to Ash Deposition,” where seawater ash and pre-eruptive chlorophyll-a concentrations can be estimated, we consider the potential bias of suspended ash taking these new findings into account.

Impact of Chaitén ash on light availability for phytoplankton

The impact of ash on $K_d(z_m, 443\text{ nm})$ is shown in **Figure 4C**. As for remote sensing estimates of chlorophyll-a described previously (Section: “Impact of Chaitén Ash on Satellite Retrieved Chlorophyll-a”), the relative impact of ash loading is much greater for low chlorophyll-a waters; e.g., $K_d(z_m, 443\text{ nm})$ is increased by a factor of >2 (or the euphotic depth is more than halved) by high ash loading ($>50\text{ mg m}^{-3}$) when chlorophyll-a is $<0.05\text{ mg m}^{-3}$ compared with $>0.5\text{ mg m}^{-3}$. The greater impact of an ash-driven reduction in light availability in oligotrophic waters is significant for interpreting satellite-detected phytoplankton responses to ash because in near-surface waters where remote sensing reflectances predominantly originate, phytoplankton are anticipated to be proximally growth-limited by a nutrient rather than light availability (Moore et al., 2013). Nevertheless, reductions in euphotic depths (i.e., the 1% light depth) of oligotrophic waters could be significant for phytoplankton populations living at greater depths (e.g., in the sub-surface chlorophyll maximum (SCM)), that are not detected by remote sensing, where the reductions may drive physiological adjustments (i.e., increases in intracellular chlorophyll-a), shifts in community structure, or a shallowing of the SCM. Such shifts could be augmented by any reduction in K_d driven by an increase in phytoplankton biomass in shallower waters as a result of nutrient fertilization from the ash.

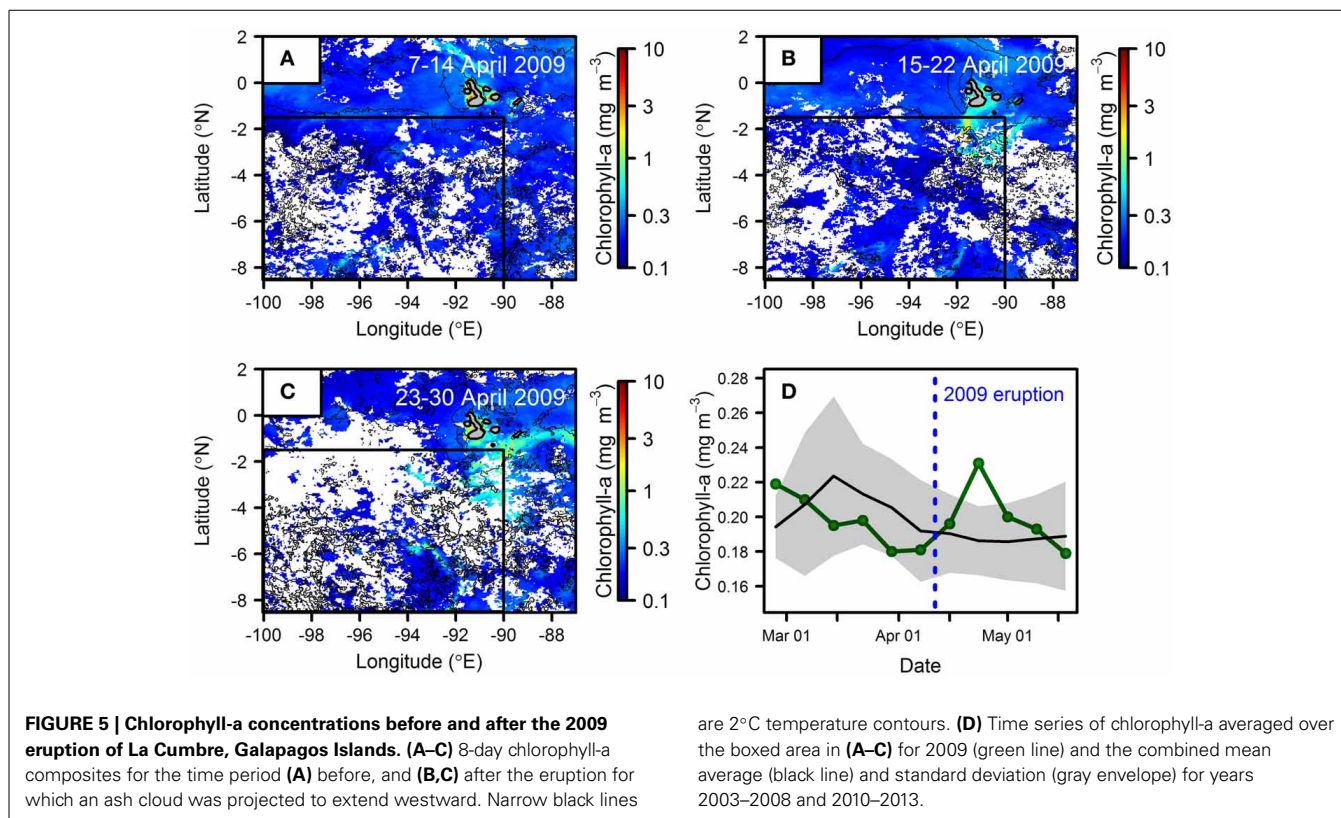
REMOTE SENSING OF PHYTOPLANKTON RESPONSE TO ASH DEPOSITION

HNLC regions

Mean satellite-derived chlorophyll-a for the month of the Kasatochi 2008 eruption, averaged for a region of ash deposition in the North East Pacific, was reported to be double that for any month since September 1997 (Hamme et al., 2010; **Figure 3A**; **Table 3**). **Figure 3B** shows initial chlorophyll-a concentrations of around 0.5 mg m^{-3} , which at least for the optical properties of the Chaitén ash (**Table 2**), suggest a relatively insignificant biasing of retrieved chlorophyll-a (**Figure 4**). Furthermore, when we plot the daily resolved chlorophyll growth rate trend we identify the increase at 5 days post-eruption [and therefore $\sim 2\text{--}3$ days after expected ash deposition (Langmann et al., 2010a,b)] (**Figure 3B**), which is (i) consistent with the timescale of chlorophyll-a response observed in mesoscale Fe enrichment experiments performed in the same region (Tsuda et al., 2003; Boyd et al., 2004), and (ii) provides strong qualitative evidence itself of ash particles in the water column not biasing chlorophyll-a concentrations significantly upwards. Eruptions of similar magnitude from Shiveluch (Kamchatka Peninsula, Russia)

and Sarychev Peak (Kuril Islands, Russia), also located in the high latitude North Pacific (**Figure 1**; **Table 3**), occurred during August 1999 and June 2009 respectively (i.e., summertime, as for Kasatochi 2008), yet our new satellite retrievals show that they produced no observable fertilization. The Shiveluch eruption coincided with onshore southeasterly winds limiting dispersal of ash over low chlorophyll-a regions of the open ocean, whilst images of aerosol loading from the Sarychev Peak eruption resulted in ash deposition over waters previously demonstrated to be Fe-limited in the same season (Tsuda et al., 2003; Fujiki et al., 2014). Unfortunately, any potential remote sensing of phytoplankton response to this latter eruption was prevented due to scarce ocean color coverage in the ash cloud region for 2 weeks subsequent to the event.

Even where detectable, attribution of a satellite-detected chlorophyll-a response to ash deposition without supporting field observations (i.e., Hamme et al., 2010; Achterberg et al., 2013) is difficult. One example is that of a relatively small (VEI 2) eruption of La Cumbre volcano on the Galapagos Islands in 2009. An ash cloud was reported to extend southwest of the island after an eruption on April 11th (Global Volcanism Program, <http://www.volcano.si.edu/>) into waters typically having elevated nitrate concentrations owing to deep-water upwelling (**Figure 1**; **Table 3**). A trio of 8-day chlorophyll-a composites show increasing concentrations to the south west of the volcano a few days after the eruption period (**Figure 5**). However, attempting to associate these subtle chlorophyll-a increases with sub-areal Fe supply is difficult, with analysis of other satellite-retrieved variables suggesting an alternative or corroboratory role of subsurface Fe supply. Specifically, the development of an increased temperature gradient within the zone of elevated chlorophyll-a between pre-/syn- and post-eruption composites (**Figures 5A–C**), 10 times enhanced wind stress over background levels on 15th April, and the development of an east-west sea surface height gradient across the islands between the **Figures 5A,B** time periods (wind and sea surface height data are not shown in the figure; see Section: “Remote Sensing Data” for data access) could be individually or collectively hypothesized to lead to enhanced Fe supply from deeper waters. Similarly, several other events from the same islands (Sierra Negra, October 22nd 2005 eruption; La Cumbre, May 2005 eruptions) displayed no chlorophyll-a responses that could readily be associated with ash deposition (**Table 3**). Furthermore, the significantly larger VEI 4 eruption of Reventador (Ecuador; see: **Figure 1**; **Table 3**) on November 2nd 2002 resulted in ash deposition in the same elevated nitrate eastern Equatorial Pacific region (e.g., Tupper et al., 2006), yet calculating a monthly averaged time series for two regions within the ash fallout area (-85°E to -80°E , 1.5°N to -1.5°N , representing waters in close proximity to the volcano; and -95°E to -80°E , 5°N to -5°N , representing a wider Equatorial Pacific area) indicated chlorophyll-a concentrations for November 2002–December 2002 to be lower (by up to $\sim 1/3$) than the MODIS 2002–2013 climatological average. However, closer inspection of satellite retrieved chlorophyll-a images shortly after the eruption revealed a consistently sparse pixel coverage effectively invalidating any area-averaged time series statistics.

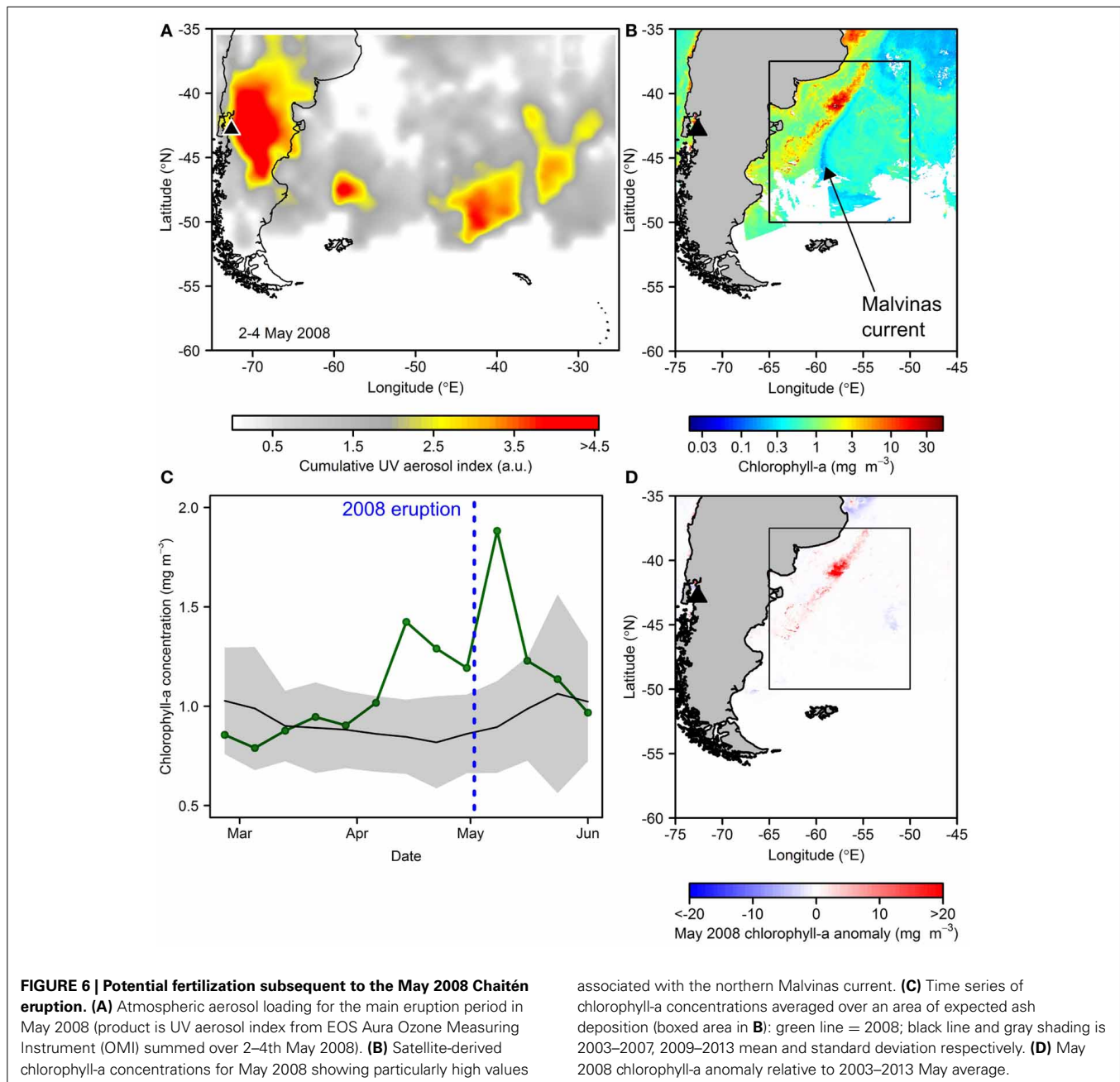


Given the status of the Southern Ocean as the largest and biogeochemically most significant HNLC region (e.g., Sigman et al., 2010), biological responses to nutrient enrichment in these waters is of particular interest (Watson, 1997; Boyd et al., 2007; Smetacek et al., 2012; Browning et al., 2014a). Furthermore, active present day South America volcanism almost certainly provides a considerable flux of ash into these waters (Gaiero et al., 2003; Watt et al., 2009). The 2008 eruption of Chaitén (Chile) was of the same scale as the Kasatochi eruption (VEI 4), and its ash cloud could be clearly distinguished as a plume moving eastwards toward the South Atlantic and Southern Ocean (Figure 6A; also, e.g., Watt et al., 2009; Durant et al., 2012). Our analysis of monthly composites of chlorophyll-a for this region revealed much elevated concentrations in waters closely associated with the Malvinas-Brazil current confluence and South American shelf (Figure 6B). Furthermore, our measurements of inherent optical properties with this same ash type (see Figure 4) suggest that the baseline chlorophyll-a concentration of $>0.5 \text{ mg m}^{-3}$ in the wider region of deposition (Figure 6B) would not be biasing this observation significantly.

Enhanced chlorophyll-a concentrations in this oceanographic feature in itself is not atypical, driven by interaction of cold, high-nitrate waters of the Malvinas Current with warmer, elevated micronutrient waters in close proximity to the South American shelf break, producing a favorable irradiance-nutrient regime for phytoplankton growth (Gayoso and Podesta, 1996; Brandini et al., 2000; Moore and Abbott, 2000; Garcia et al., 2004; Rivas et al., 2006). However, the satellite-derived chlorophyll-a concentrations for this zone in May 2008, the month of the

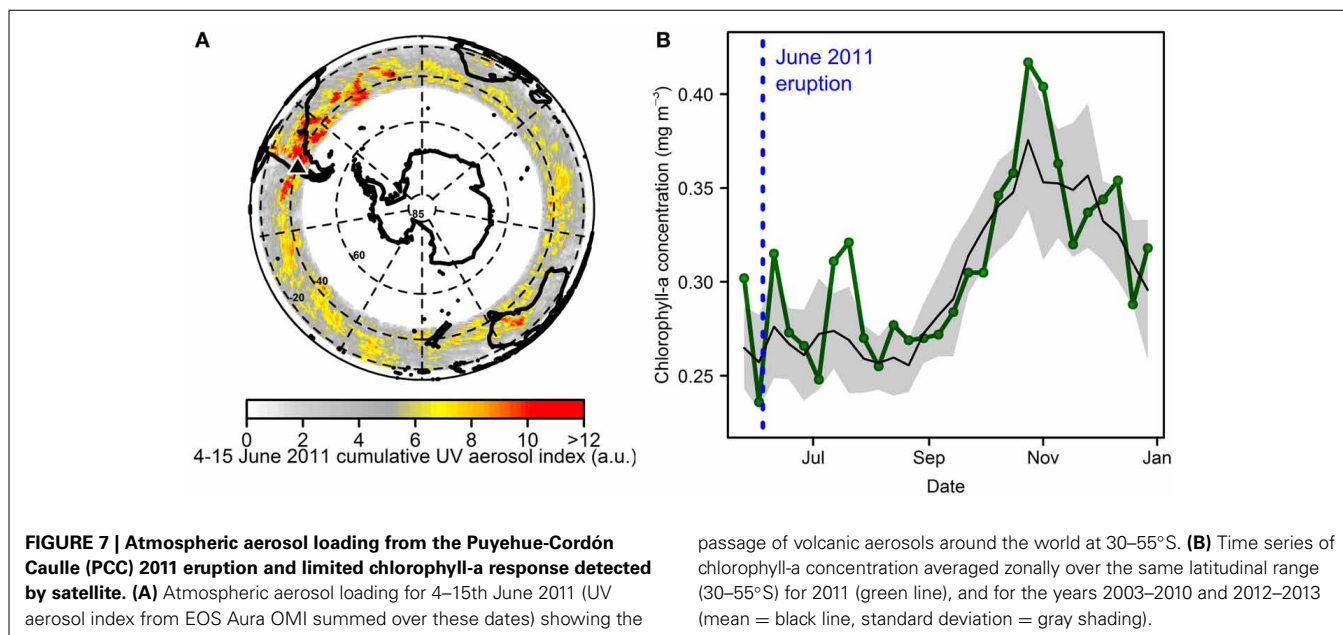
Chaitén eruption (main eruption: 2–10 May), exceeded the 2003–2013 May climatological average by up to $\sim 45 \text{ mg m}^{-3}$, and $>10 \text{ mg m}^{-3}$ over a wider ocean area (Figure 6D). Inspecting maps of inferred atmospheric aerosol loading suggested the ash deposition area to be to the south of this high chlorophyll-a anomaly (Figure 6A), yet rapid advection of these potentially micronutrient-enriched waters northwards in the Malvinas current could be hypothesized to play some role sustaining this anomalously high phytoplankton stock. When averaged over an area of potential ash deposition for 8-day chlorophyll-a composites before and after the eruption, the 2008 time series also showed the post-eruption period to be elevated relative to a climatological average (Figure 6C); however, a pre-eruption increasing trend suggests an alternative driver for bloom initiation. Moreover, the close association of the anomalous bloom with the dynamic Malvinas current and particularly the shelf break region, where a number of anomalous physical oceanographic phenomena could be hypothesized to alter the growth environment for phytoplankton in this year, once again complicates interpretation of this event from remote sensing data alone.

As for case studies discussed previously, any indication of a response to ash deposition from other South American eruptions is not always either found or readily observable in satellite images. For example, we found that a vigorous explosive eruption of Llaima (Chile) in January 2008, that would have led to light ash deposition in roughly the same region as from the Chaitén 2008 event, was not followed by any apparent response in satellite-retrieved chlorophyll-a (Table 2). This was the case even though the event occurred during mid-austral summer, and thus



potentially a time period of elevated Fe stress. If the Chaitén 2008 event indeed had any causative link with the observed enhanced chlorophyll-a biomass in the Argentine Basin, the smaller eruption magnitude (VEI 3) of Llaima 2008 and the resultant lower ash loading could offer an explanation for the absence of any observable satellite-detected chlorophyll-a response to this event. More recently, the Puyehue-Cordón Caulle (PCC) volcano in Chile erupted in June 2011 with a much larger eruption volume than Chaitén or Llaima in 2008 (VEI 5, see **Table 3**). An ash cloud was observed in images of atmospheric aerosol loading to extend into the South Atlantic and even circumnavigating the globe at 30–55°S (e.g., Collini et al., 2013; **Figure 7A**). Peak ash

deposition occurred in winter when light availability was likely the dominant limiting resource for phytoplankton, with Fe stress status uncertain (Boyd, 2002). Furthermore, due to the limited incident solar irradiance at this time of year, satellite-retrieved ocean color data were limited to latitudes north of 45°S for July–August. Assessment of short-term (1–2 month) phytoplankton responses in the Southern Ocean was therefore restricted to lower latitudes. Inspection of a time series of 8-day chlorophyll-a composites—averaged zonally over the latitudinal range that both had ocean color coverage and expected ash deposition—revealed a chlorophyll-a increase above that of the climatological mean and standard deviation shortly after the deposition event



(Figure 7B). However, significant subsequent chlorophyll-a variability about the mean indicates that, despite the significant Fe loading anticipated, it is clearly not possible to associate changes in phytoplankton standing stock with ash supply with any degree of confidence.

LNL regions

Lin et al. (2011) reported a remote sensing analysis of phytoplankton response in the North Pacific subtropical gyre subsequent to the Anatahan 2003 eruption. Citing prior work suggesting a potential influence of ash on satellite retrieved chlorophyll (Claustre et al., 2002; Duggen et al., 2007), Lin et al. (2011) noted that the observed chlorophyll-a concentration increase of $0.4\text{--}0.8\text{ mg m}^{-3}$, 8–16 times greater than surrounding waters ($\sim 0.05\text{ mg m}^{-3}$), could have been partially biased by ash loading of surface waters. Our optical measurements on Chaitén ash (Figure 4) suggest that, given the low initial chlorophyll concentrations, estimated chlorophyll-a could have been biased on the order of ~ 10 -fold higher than surrounding waters subsequent to ash contamination; thus having the potential to fully account for the satellite-retrieved chlorophyll anomaly without any increase in phytoplankton biomass (again, this assumes that the optical properties of rhyolitic Chaitén ash are suitable to apply to the brown-gray andesitic Anatahan ash). However, a continued chlorophyll response at a time period ~ 7 days after ash deposition, and thus potentially after a significant fraction of ash sinking below surface waters (Duggen et al., 2007), would suggest that this probably not the case.

Uematsu et al. (2004) reported small monthly-averaged satellite-derived chlorophyll-a enhancements ($<0.02\text{ mg m}^{-3}$) in initially oligotrophic waters ($<0.08\text{ mg chlorophyll-a m}^{-3}$) subsequent to the Miyake-jima 2000 eruption (Tables 1, 3). Similarly to Anatahan the optical experiments reported here for Chaitén ash (Figure 4), suggest that, if applicable to basaltic ash, these enhancements could have been driven entirely by ash-mediated

passage of volcanic aerosols around the world at $30\text{--}55^\circ\text{S}$. (B) Time series of chlorophyll-a concentration averaged zonally over the same latitudinal range ($30\text{--}55^\circ\text{S}$) for 2011 (green line), and for the years 2003–2010 and 2012–2013 (mean = black line, standard deviation = gray shading).

changes in ocean color (note that Uematsu et al., 2004, used SeaWiFS images processed using a similar blue:green reflectance ratio algorithm as MODIS).

We carried out an investigation into several additional volcanic ash deposition events in LNL waters and found no indication of phytoplankton responding to ash supply. For example, the VEI 4 eruption of Ulawun (Papua New Guinea) in 2000 was larger than the Anatahan (2003) eruption reported in the study of Lin et al. (2011), and was coincident with SE winds resulting in ash deposition over near-coastal low chlorophyll waters in the Western Pacific (October 2000 SeaWiFS chlorophyll-a $<0.08\text{ mg m}^{-3}$), yet no clear chlorophyll-a response was readily detectable in satellite images (Table 3). The relatively high anticipated ash flux into low chlorophyll-a waters and no detection of a chlorophyll-a response suggests little ash-driven bias in estimated chlorophyll-a concentrations; indicating either a divergence in optical properties of the basaltic-andesitic Uluwan ash relative to the rhyolitic Chaitén ash we have tested, or a limited residence time of ash in surface waters. A series of explosive (VEI 4) eruptions have occurred in Indonesia and Papua New Guinea since 2002 (Table 3; Figure 1): Ruang (2002); Manam (2004); Rabaul (2006); Merapi (2010); and Kelud (2014). However, the Ruang, Manam, Rabaul eruptions were accompanied by unfavorable winds for seaward ash deposition, and inspection of satellite-derived chlorophyll-a concentrations subsequent to ash deposition from Merapi and Kelud in the west Indian Ocean revealed very poor retrieval of ocean color data in the expected deposition region (presumably due to high incidence of midday cloud cover and potentially the influence of the ash cloud itself) hindering observation of any potential phytoplankton response.

Future directions for remote sensing of phytoplankton responses

The analysis reported in this section has highlighted difficulties with detecting any potential phytoplankton response to ash deposition events using satellite remote sensing. In a number of cases

this was due to poorly defined or limited seaward ash deposition, restricted temporal or spatial resolution of satellite coverage, or the potential confounding effect of suspended ash on the optical properties of the water column itself (Table 3). Cases however where chlorophyll-*a* biomass increases were detected with confidence, for example La Cumbre 2009 (Figure 5), Chaiten 2008 (Figure 6), and Eyjafjallajökull 2010 (Achterberg et al., 2013; Henson et al., 2013), also remain difficult to unambiguously associate with ash nutrient fertilization as a result of multiple potential alternative or additional drivers. Tackling the latter may be aided by continued refinement and ground-truthing of remote sensing methodologies for observing phytoplankton physiology as a less ambiguous measure of nutrient fertilization than changes in phytoplankton biomass (Westberry et al., 2013). Although requiring additional research to begin using with confidence for this purpose, changes in chlorophyll-*a* fluorescence quantum yields with Fe stress status hold promise (Behrenfeld et al., 2009; Westberry et al., 2013; Browning et al., 2014b). Observing changes in Fe stress could overcome limitations with the use of chlorophyll-*a* biomass to either elucidate any phytoplankton response to ash deposition where no change in biomass is observed, or to deconvolve the driving mechanism behind an observed biomass response (i.e., a physiological signal of Fe stress recovery followed by a biomass response would be most consistent with ash fertilization). Observing physiological changes that are transitioning more rapidly in response to a transient supply of nutrients than changes in biomass may however require a higher temporal resolution of satellite images that, depending on the region and season of interest, are often not readily available.

CARBON SEQUESTRATION POTENTIAL OF VOLCANIC ASH DEPOSITION EVENTS

Alongside ash, volcanic eruptions release CO₂ into the atmosphere. However, even during periods of increased volcanism the amount is thought to be relatively small on geologically short (10³–10⁴ year) timescales and not of great significance in comparison with the atmospheric reservoir of carbon (e.g., Self et al., 2006). Ocean fertilization can increase rates of net organic matter synthesis, which upon sinking to the deep ocean, effectively represents an export of atmospheric carbon (Watson et al., 2000). Accordingly, previous studies have pointed out the potential significance of oceanic volcanic ash fertilization for regulating atmospheric carbon in the past (Spirakis, 1991; Bains et al., 2000; Bay et al., 2004; Cather et al., 2009). Recent observations—both in terms of volcanic ash Fe release experiments and mesoscale Fe enrichments—provide valuable constraints on evaluating the potential role of volcanic fertilization carbon feedbacks in the earth system.

Extrapolating the pCO₂ reduction observed at OSP led Hamme et al. (2010) to estimate an atmospheric drawdown of ~0.01 Pg C resulting from the Kasatochi 2008 fertilization event, which for comparison represents just ~0.5% of the anthropogenic CO₂ estimated to be taken up each year by the ocean (Manning and Keeling, 2006). Similarly, atmospheric carbon removal subsequent to the Eyjafjallajökull 2010 eruption was suggested to be minimal by Achterberg et al. (2013), the major reason being the relatively modest unutilized macronutrient inventory

that typically characterizes the post-bloom condition in the North Atlantic. Thus, in this particular biogeochemical system, any increase in Fe supply would be hypothesized to drive a rapid transition from Fe- to macronutrient-limitation (Ryan-Keogh et al., 2013). Atmospheric carbon removal by the biological pump is expected to scale with macronutrient drawdown (Sigman and Boyle, 2000), thus the high macronutrient waters of the Southern Ocean currently have the greatest potential for carbon sequestration subsequent to volcanic Fe input (Watson, 1997; Browning et al., 2014a).

Volcanoes of present-day southern Chile and Patagonia likely represent a significant fraction of the total volcanic ash flux to the Southern Ocean. Using a volcanic Fe supply of 50–500 Gg from these volcanoes over the past 16.5 kyr (following assumptions in Section: “Calculations of Potential Bounds for Ash-Fertilized Carbon Export”), alongside an empirically constrained range of carbon export efficiencies (Section: “Calculations of Potential Bounds for Ash-Fertilized Carbon Export”), we calculate a Southern Ocean carbon export of ~0.04–15 Pg C (Figure 8A). This huge range, which accounts for the variability in two poorly constrained parameters (ash Fe release and carbon export efficiencies), highlights the considerable uncertainty that must be taken into account when attempting to evaluate volcanic Fe fertilization in the past (e.g., Bains et al., 2000; Bay et al., 2004; Cather et al., 2009; Jicha et al., 2009; Langmann, 2014). An obvious question is how does the volcanic Fe flux compare with conventional Patagonian dust over the same time period? Given Patagonian dust can itself be remobilized volcanic ash (Watt et al., 2009; Wilson et al., 2011), decoupling the two sources is complicated. However, for brevity simply using the ~40 Tg yr⁻¹ Patagonian dust flux modeled by Li et al. (2008) alongside bulk Fe contents of ~4 wt% (Gaiero et al., 2003), an assumption of no interannual variability, and lastly a dust Fe solubility range of 0.2–10% (after Baker and Croot, 2010), produces an integrated Patagonian dust Fe flux range of 0.05–2.5 Pg Fe for the last 16.5 kyr. This is 100–50,000 times greater than that of our (conservative) estimate for Patagonian volcanic Fe.

Refining estimates of Fe release and carbon export efficiencies could be aided by detailed observations of contemporary eruptions. Mount Hudson erupted in 1991 resulting in heavy ash fallout in the South Atlantic and Southern Ocean (Figure 9; Gaiero et al., 2003), with Fe supply from this single eruption calculated as ~6.5% that of our conservative estimate of 16.5 kyr-present day volcanic fluxes (see Section: “Calculations of Potential Bounds for Ash-Fertilized Carbon Export”). The eruption occurred in mid-austral winter (August) when phytoplankton in Southern Ocean waters are limited to first order by light availability (Boyd, 2002). However, much of the deposited Fe could well have been transported north, either in the Malvinas current or the northerly limb of the Antarctic Circumpolar Current (ACC), reaching the Atlantic subtropical frontal zone by austral spring-summertime. This frontal zone is host to Fe-stressed phytoplankton in austral summer (Browning et al., 2014c), likely making it highly sensitive to pre-bloom micronutrient loading. No ocean color sensors were in operation at this time but records of O₂/N₂ in both hemispheres indicate an O₂ pulse from southern hemisphere oceans, and thus enhanced

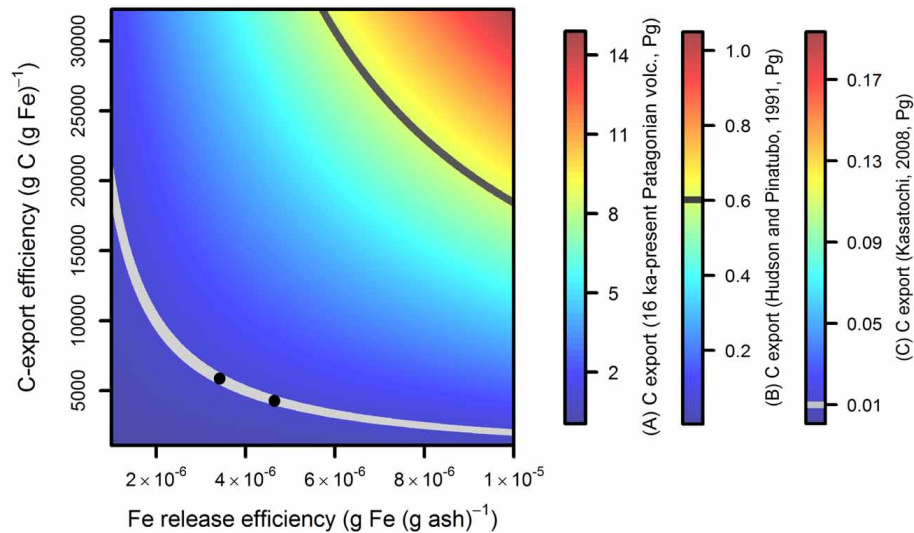


FIGURE 8 | Potential range of carbon sequestration calculated for applied bounds of Fe release from ash and carbon sequestration efficiency—highlighting the substantial uncertainty in estimating the potential for ash fertilization-induced carbon export. Ranges of Fe release and carbon sequestration efficiencies are described in Section: “Calculations of Potential Bounds for Ash-Fertilized Carbon Export.” These ranges have been applied to three estimates of ash fluxes to HNLC waters: **(A)** the 16.5 kyr to present day flux to the Southern Ocean; **(B)** the 1991 eruptions of Pinatubo and Hudson; and **(C)** the 2008 Kasatochi

eruption. Gray lines on the main figure and **(B,C)** correspond to the carbon export that would produce (i) the observed O_2 pulse from southern hemisphere oceans in 1991/1992 subsequent to the Hudson and Pinatubo events (Keeling et al., 1996) (dark gray); and (ii) the extrapolated surface ocean dissolved pCO_2 reduction at Ocean Station Papa subsequent to the Kasatochi event (Hamme et al., 2010) (light gray). Black dots on the Kasatochi curve correspond to upper and lower Fe release bounds measured from Kasatochi ash by Olgun et al. (2013b) (reported as 61–83 nmol Fe (g ash) $^{-1}$).

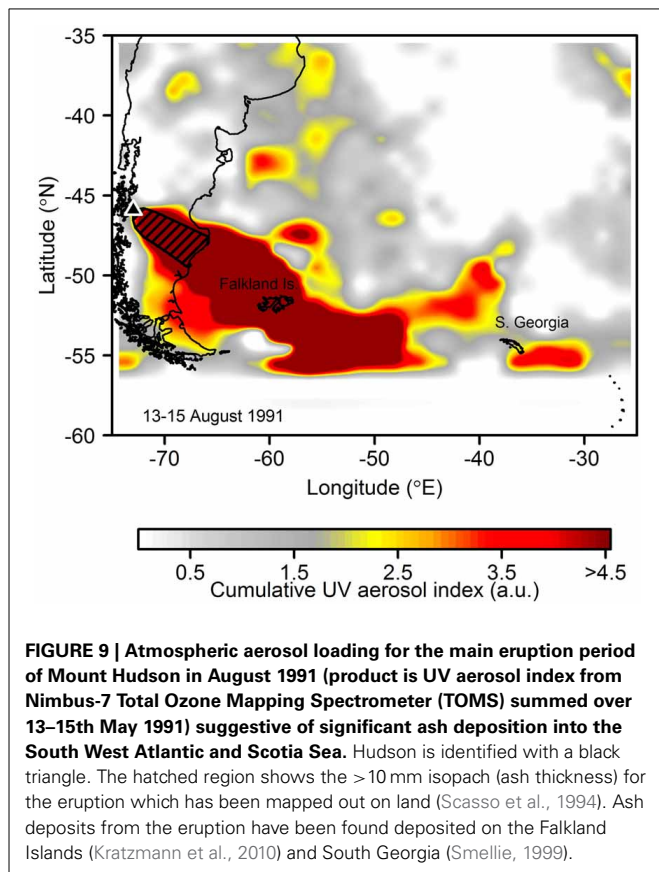


FIGURE 9 | Atmospheric aerosol loading for the main eruption period of Mount Hudson in August 1991 (product is UV aerosol index from Nimbus-7 Total Ozone Mapping Spectrometer (TOMS) summed over 13–15th May 1991) suggestive of significant ash deposition into the South West Atlantic and Scotia Sea. Hudson is identified with a black triangle. The hatched region shows the >10 mm isopach (ash thickness) for the eruption which has been mapped out on land (Scasso et al., 1994). Ash deposits from the eruption have been found deposited on the Falkland Islands (Kratzmann et al., 2010) and South Georgia (Smellie, 1999).

ocean primary productivity in these waters, during austral summer 1991/1992 (Keeling et al., 1996; Watson, 1997). This has previously been linked with Fe fertilization from the June 1991 eruption of Mt Pinatubo alone (Watson, 1997). Pinatubo is located in the northern hemisphere (Figure 1), and as noted by Langmann et al. (2010a) and Langmann (2014), considerably less ash fallout in the Southern Ocean occurred for this event.

Accordingly, performing a carbon export calculation (Section: “Calculations of Potential Bounds for Ash-Fertilized Carbon Export”) based on the erupted ash mass reaching the Southern Ocean from both Pinatubo and Hudson in 1991, produces a range of ~ 0.003 – 1 Pg C (Figure 8B). Falling within our uncertainty range, an anomalous carbon export of ~ 0.6 Pg driven by enhanced Fe fertilization would have been required to account for the whole reported $\sim 10^{14}$ mole O_2 pulse from southern hemisphere oceans in this year (Keeling et al., 1996; dark gray line on Figure 8B). Performing similar calculations, a carbon sink of ~ 0.01 Pg C from the Kasatochi 2008 eruption (extrapolated from direct measurements, Hamme et al., 2010), for an estimated eruption mass of ~ 0.6 Pg (Langmann et al., 2010a,b), offers additional potential constraint on Fe release and carbon export efficiencies (Figure 8C). Moreover, if the results of recent leaching experiments performed on Kasatochi ash by Olgun et al. (2013b) can realistically be applied (see Baker and Croot, 2010), carbon sequestration efficiency can potentially be narrowed down to ~ 5000 g C (g Fe) $^{-1}$ for this Fe enrichment (Figure 8).

We have used simple calculations to estimate volcanic Fe supply from Patagonia to be 100–50,000 times lower than that of dust estimates over long (>10 kyr) timescales. In addition to

total fluxes, differences in modes of delivery could be particularly important for Southern Ocean biogeochemistry. Volcanic deposition is dominated by transient pulses whereas dust supply is somewhat more continuous; the former likely leading to both reduced Fe release and carbon export efficiencies than continuous low-level supply (Baker and Croot, 2010; Le Moigne et al., 2014). Thus, on thousands of year timescales, ash-fertilized carbon export from Patagonian volcanism is likely orders of magnitude lower than dust, whilst individual eruptions could likely feature significantly at the interannual scale. This issue of timescale will be important to recognize in any future carbon cycle modeling that includes volcanic Fe fluxes to the ocean.

CONCLUSIONS AND FUTURE DIRECTIONS

- Bottle-scale ash enrichment experiments and observations of a suite of biogeochemical parameters subsequent to two recent ash deposition events have demonstrated phytoplankton responses in three seasonally Fe-limited regions (high latitude North Atlantic: Achterberg et al., 2013; North Pacific: Hamme et al., 2010; Mélançon et al., 2014; Southern Ocean: Browning et al., 2014a). Recorded responses to ash have been similar (Mélançon et al., 2014), smaller (Achterberg et al., 2013), or greater than (Browning et al., 2014a) that of Fe-only enrichments. From the limited observations available, these differences appear to depend more on the biogeochemical system rather than particular ash type. Remote sensing of an eruption in the highly-oligotrophic macronutrient-limited subtropical Pacific has provided evidence for the stimulation of a phytoplankton bloom (Lin et al., 2011), consistent with recent field observations of large-scale biogeochemical patterns responding to dust deposition in the (sub)tropical North Atlantic (Schlosser et al., 2014).
- Measurements of inherent optical properties of Chaitén ash suspended in seawater suggest that satellite-retrieved chlorophyll-a concentrations can be biased high by greater than an order of magnitude. The magnitude and sign of bias is however highly sensitive to the respective ash loading and initial seawater chlorophyll-a concentration. Experiments of inherent optical properties for other ash types including ranges of ash particle size spectra, alongside an improved sensitivity for measuring the magnitude and spectral variability of light absorption by ash are needed to better constrain biasing by ash-loading for chlorophyll-a estimated using current Case 1 ocean color algorithms. Beyond a simple adjustment of routine Case 1 algorithms, new algorithms similar to those being developed for optically complex Case 2 waters (Odermatt et al., 2012) could be investigated as a more rigorous means for accurate chlorophyll-a retrieval. Such algorithms could make use of the greater range of wavebands available on current and future ocean color sensors for isolating ash signals.
- Phytoplankton responses to ash deposition are not consistently observed using remote sensing. Often poor temporal and spatial satellite coverage during an expected response period may simply be preventing detection, yet there are multiple factors responsible for regulating the phytoplankton standing crop that should be anticipated to potentially result in the absence of biomass increase subsequent to a nutrient enrichment event (Cullen et al., 1992; Boyd et al., 2010). Continuous low-level input of ash through small, regular eruptions likely fertilizes phytoplankton to some extent, potentially with greater efficiency (Baker and Croot, 2010; Le Moigne et al., 2014), although responses to these can be difficult to identify using remote sensing. New algorithms relating subtle changes in chlorophyll-a biomass (e.g., over baseline averages) to potential nutrient supply could offer a means to better resolve these (O'Malley et al., 2014).
- Continued refinement and ground-truthing of remote sensing methodologies for observing phytoplankton physiology as a less ambiguous measure of nutrient fertilization than phytoplankton biomass may better enable detected responses to be causatively associated with a transient ash deposition event. For example, changes in chlorophyll-a fluorescence quantum yields with Fe stress status (Behrenfeld et al., 2009; Westberry et al., 2013; Browning et al., 2014b) could overcome limitations with the use of chlorophyll-a biomass to elucidate any phytoplankton response to ash deposition or to deconvolve the driving mechanism behind any biomass response. Improvements in quantitatively estimating ash concentrations in eruption plumes using remote sensing will help refine estimates of ash fluxes to the ocean (e.g., Prata and Prata, 2012; Webster et al., 2012).
- Volcanic eruptions have the potential to cause regional or even global-scale Fe-fertilization (e.g., Duggen et al., 2010; Langmann, 2014). However, whilst the ecological consequences of such fertilization events will almost certainly be large, there is much uncertainty with regard to potential atmospheric carbon sequestration from these.
- Carefully designed experiments detecting metal release from ash using conditions that best replicate, or ideally utilize, the natural ocean will be an invaluable resource for constraining the fertilization potential of eruptions. Following the lead of studies performing leaching experiments on regular desert dust (e.g., Baker and Croot, 2010), such experiments should also pay careful consideration to ash particle size, ash-loading, and exposure time to best mimic natural ash depositions in the oceanic regime of interest (i.e., coastal vs. open ocean waters) (Duggen et al., 2010).
- Large-scale ash deposition events potentially provide a useful platform to assess the response of a biogeochemical system to relief of micronutrient stress (Hamme et al., 2010; Achterberg et al., 2013). With better characterization of micronutrient release, such events could be perhaps be more suited to this purpose than dust deposition, as eruptions are point sourced and contain diagnostic gasses, aiding identification of event and response using remote sensing. Given the often sporadic and remote nature of eruptions and ash deposition, sensors on autonomous platforms (Johnson et al., 2009; Hamme et al., 2010) could be essential in providing the independent ground observations needed to compliment remote sensing in detecting and quantifying biogeochemical responses. The international oceanographic community might also wish to consider putting contingency plans in place in order to be able to respond rapidly with a full suite of relevant biogeochemical measurements to any eruption event that is within reach of any fortuitously located research vessel.

AUTHOR CONTRIBUTIONS

All authors contributed to the project design. KS and VV performed the ash optics experiments. TB and VV analyzed the ash optics data. TB and KS performed the remote sensing analysis. TB synthesized the review material and wrote the initial draft of the paper and all authors contributed to its revision.

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