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# The ocean response to volcanic iron fertilisation after the eruption of Kasatochi volcano: a regional scale biogeochemical ocean model study

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## Abstract

In High-Nutrient-Low-Chlorophyll regions, phytoplankton growth is limited by the availability of water soluble iron. Volcanic ash can carry bio-available iron salts on its surface, which may be formed during volcanic eruptions by surface reactions between volcanic gases and ash. The eruption of Kasatochi volcano in August 2008 led to ash deposition into the iron-limited NE Pacific Ocean releasing iron upon contact of volcanic ash with seawater. Atmospheric and oceanic conditions were favourable to generate a massive phytoplankton bloom, which was observed by satellite instruments and in-situ measurements. Here we investigate this event with a regional scale ocean biogeochemical model system to illuminate the ocean response to iron fertilisation by volcanic ash. The results indicate that the added iron triggered an additional phytoplankton bloom in the summer of 2008, which produced a drawdown of carbon dioxide in surface seawater. The simulated development is in good agreement with the available observations.

## 1 Introduction

In “High-Nutrient-Low-Chlorophyll” (HNLC) oceanic regions, like the Southern Ocean, the Equatorial and North-East Pacific, macronutrient concentrations are usually high. Phytoplankton growth is however limited by the availability of water soluble iron (Martin and Fitzwater, 1988). Only during winter time the availability of sunlight represents the major limiting factor. Generally, mineral dust is assumed to represent the major external source of bio-available iron for the open ocean (e.g. Jickels et al., 2005). In addition, other external sources like volcanic ash as a carrier of bio-available iron have recently been identified (e.g. Frogner et al., 2001; Duggen et al., 2007; Jones and Gislason, 2008). After the eruption of Kasatochi volcano on the Aleutian Islands in August 2008, volcanic ash was deposited into the iron-limited oceanic NE Pacific where atmospheric and oceanic conditions were favourable to generate a massive phytoplankton bloom as observed by satellite instruments (Langmann et al., 2010a) and in-situ measurements

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(Hamme et al., 2010). The physico-chemical mechanisms behind the processes contributing to bio-available iron production on volcanic ash surfaces in volcanic plumes, where the ash undergoes temperature regimes from about 1000 °C to ambient temperature, are still largely unknown (Ayres and Delmelle, 2012). Therefore, laboratory leaching experiments provide the major information on the bio-availability of iron from volcanic ash (e.g. Duggen et al., 2007; Olgun et al., 2011). Although these experiments reveal a large variability of the release rate of bio-available iron from volcanic ash, they showed that iron bio-availability from volcanic ash surfaces is in the same range than that of mineral dust. But the amount of volcanic ash deposited into the surface ocean within a few days immediately after a volcanic eruption may exceed that of mineral dust by orders of magnitude (e.g. Gaiero et al., 2003), thus pointing to the need to improve our knowledge on the processes and impacts associated with volcanic ash fertilisation of the surface ocean.

We investigated the ocean fertilisation event after the eruption of Kasauchi in August 2008 with a regional scale ocean biogeochemical model. As only limited in-situ measurements are available, our modelling study may contribute to a better understanding of the NE Pacific biogeochemical response after being iron-fertilised by Kasatochi ash. In addition, this study may illuminate the potential connection between the huge number of sockeye salmons returning to the Fraser River in Canada in 2010 (Jones, 2010) and the iron-fertilisation of the NE Pacific by Kasatochi ash in 2008. An improved understanding of such a connection is of considerable economic interest for the fishery industry. The volcanic eruption of Kasatochi is briefly summarised in Sect. 2. Section 3 describes the ocean biogeochemical model used for this study. Section 4 presents model results and comparisons with observations. Further model sensitivity experiments are discussed in Sect. 5 before conclusions and an outlook are given in Sect. 6.

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## 2 Kasatochi volcanic eruption

Kasatochi volcano (52.17° N, 171.51° W) erupted on 7 August 2008. Three major explosive events occurred with eruption plumes rising to altitudes of about 15 km (Waythomas et al., 2010). The last explosive event on 8 August, which lasted for about 17 h contained the highest amount of volcanic ash (Waythomas et al., 2010). The ash cloud formed a counter-clockwise spiral at altitudes between 9 km and 14 km and spread further eastward across the NE Pacific (Fig. 1) (Langmann et al., 2010a). Using an atmosphere-aerosol model, the release, dispersion and deposition of the Kasatochi ash was determined by Langmann et al. (2010b). Based on the modeled tephra fallout, they estimated the amount of iron supplied to the NE Pacific ocean attached to the volcanic ash from Kasatochi. Assuming an ocean mixed layer depth of 30 m (Whitney and Freeland, 1999) and a release of 200 nmol Fe per gram volcanic ash (a typical value for subduction zone volcanoes; see Olgun et al., 2011) the resulting surface ocean iron concentration at Papa (Fig. 2a) is between 1–2 nmol l<sup>-1</sup>. Associated daily ash fluxes to the ocean are displayed in Fig. 2b. Results from mesoscale iron enrichment experiments show that an increase of surface ocean iron concentrations by 2–3 nmol l<sup>-1</sup> is sufficient for large diatoms to grow rapidly in iron-limited regions (Wells, 2003) such as the NE Pacific.

## 3 Ocean biogeochemical model description

The ECOHAM4 (Ecosystem Model, Hamburg, Version 4) model (e.g. Pätsch et al., 2008; Lorkowski et al., 2012) has been developed at the Institute of Oceanography at the University of Hamburg. It is a regional scale three-dimensional ocean biogeochemistry model, coupled to the hydrodynamic model HAMSOM (Backhaus, 1985). ECOHAM has mainly been applied over the Northwest European continental shelf area. The model is able to simulate the biogeochemical cycles of carbon, oxygen, nitrogen, phosphate and silicate. To complete the carbon cycle a carbonate chemistry model is

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included. Pelagic prognostic variables in the water column are e.g. two kinds of phytoplankton (diatoms and flagellates), zooplankton, bacteria and two kinds of detritus (fast and slow sinking). Iron limitation does not play a role in this region.

For applications of ECOHAM in HNLC areas, an iron cycle model has been newly implemented, which considers the direct influence of iron addition to the euphotic zone for diatoms and flagellates (Fig. 3). The growth of phytoplankton is now limited not only by light, nitrogen, phosphate, and in case of diatoms by silicate, but also by the availability of iron. The iron is recycled via the different detritus pools (Fig. 3). Due to the influence on primary production, the iron may also indirectly influence the zooplankton biomass as well as the resulting carbon dioxide concentration. In this model approach the assumption is made, that all dissolved iron in the first meters of seawater is bio-available for phytoplankton uptake. The parameterisation of biogeochemical iron dynamics used here is very similar to those in other currently applied three-dimensional ocean biogeochemical models (e.g. Aumont et al., 2003; Denman et al., 2006; Gregg et al., 2003; Lancelot et al., 2000; Moore et al., 2004). Despite their simplicity, these iron parameterisations proved to be able to reproduce the main biogeochemical patterns of the ocean (Boyd and Ellwood, 2010).

Meteorological forcing data of cloud cover, precipitation, solar irradiation, near surface relative humidity, temperature, wind speed and direction for the year 2008 are taken from the ECMWF analysis data base (<http://cera-www.dkrz.de/WDC/oi/Index.jsp>). We assume initial macronutrient concentrations in the surface water based on climatological means of the WOCE data base (<http://www.nodc.noaa.gov/OC5/SELECT/woaselect/woaselect.html>) in the NE Pacific Ocean: nitrate:  $10.7 \mu\text{mol N l}^{-1}$ , phosphate:  $1.3 \mu\text{mol P l}^{-1}$ , silicate:  $20.5 \mu\text{mol S l}^{-1}$  and 32 psu for the salinity. For the initialisation of iron we assume a concentration of  $0.2 \text{ nmol Fe l}^{-1}$  in the upper 150 m of the ocean and a concentration of  $0.6 \text{ nmol Fe l}^{-1}$  below the surface layer based on Aumont et al. (2003). Half-saturation constants of iron for diatoms ( $0.188 \text{ nmol Fe l}^{-1}$ ) and nanophytoplankton ( $0.0333 \text{ nmol Fe l}^{-1}$ ) are taken from Denman et al. (2006) who carried out model simulations during the SERIES fertilisation experiments in the NE Pacific.

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We focus here on one-dimensional column applications around the buoy Papa (50° N, 145° W) although the model is set-up in three-dimensions. The water column is subdivided into 24 vertical layers of increasing thickness with depth, with the upper 50 m consisting of eight layers of 5 m depth and an upper layer of 10 m depth. The annual cycle of the mixed layer depth is prescribed according to data from Whitney and Freeland (1999). Below the mixed layer, vertical diffusion coefficients are set to  $0.134 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ . They reach maximum values of  $0.035 \text{ m}^2 \text{ s}^{-1}$  close to the surface. Sea surface temperature varies between 5 °C during winter and 13 °C during summer. Comparing temporal and horizontal scales it appears appropriate to neglect horizontal advection and diffusion in this column model study. The standard experiment described in Sect. 4 assumes an iron input associated with volcanic ash of  $24 \times 10^3 \text{ nmol Fe m}^{-2}$  at Papa within the three days of 9–11 August 2008. The model is run for two years, with the first year serving as spin-up time.

#### 4 Model results and comparison with observations

The analysis of the ECOHAM model results focuses on the nutrient, phytoplankton, zooplankton, CO<sub>2</sub> and pH development in the NE Pacific Ocean following the iron release from volcanic ash after the eruption of Kasatochi. We compare model results at the station Papa in the upper 50 m of the ocean of simulations without and with iron fertilisation. We note that we focus on the influence of iron released from volcanic ash on the biogeochemistry of the ocean because a full evaluation of the biogeochemical model results is beyond the scope of this manuscript.

Phytoplankton growth at Papa, which is shown in Fig. 4 from January to December 2008 begins in spring reaching about  $10 \mu\text{mol C l}^{-1}$  during April. Due to iron consumption and limitation, the spring bloom declines during summer. Upon iron deposition associated with volcanic ash deposition on 8–11 August a considerable increase in phytoplankton concentration (about  $8 \mu\text{mol C l}^{-1}$ ) starts a few days later. This bloom lasted for several weeks and it is therefore in good agreement with the measurements

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(Langmann et al., 2010; Hamme et al., 2010). Without iron deposition, phytoplankton concentration remains at about  $2 \mu\text{mol C l}^{-1}$  during late summer/early autumn.

Usually, macronutrients are available in high concentrations in the HNLC area of the NE Pacific Ocean. During late autumn and winter the mixed layer concentrations are high due to efficient mixing with the deeper ocean layers (Fig. 5). During the spring bloom, macronutrient mixed layer concentrations decrease and stay at a constant level during summer when the ocean mixed layer depth is restricted to about 20–40 m (Whitney and Freeland, 1999). With volcanic ash deposition in August 2008, when phytoplankton growth is no longer limited by the availability of iron, macronutrient concentrations are further depleted (Fig. 5). Hamme et al. (2010) measured a distinct decrease in silicate at Papa. However, it remains uncertain if and which macronutrient concentration becomes limiting for phytoplankton growth as in the model simulations this is dependent on the prescribed initial concentration. Release of silicate, phosphate, nitrate and ammonium from Kasatochi ash contributes in the nano molar range (Olgun et al., 2012) and can thus be regarded as negligible.

Zooplankton biomass builds up with a delay of some weeks after the deposition of volcanic ash (Fig. 6). According to Hamme et al. (2010) meso-zooplankton abundances were dominated by large copepods. Their organic material fills mainly in the heavier faecal pellets feeding mainly into the fast sinking detritus. High diatom abundances may also have increased export by increasing the density of sinking particles thereby slightly decreasing atmospheric  $\text{CO}_2$  by  $\sim 0.01 \text{ Pg C}$  (Hamme et al., 2010).

The simulated pH varies between 7.99 and 8.05 throughout the year at station Papa (Fig. 7). In August 2008, it increases from 8.01 to 8.05 after fertilisation with iron. This is in good agreement with in-situ measurements by Hamme et al. (2010) – although modelled values are slightly smaller – who reported a measured pH increase of 0.06 from 8.08 to 8.14. Increasing pH values and a decreasing  $\text{CO}_2$  partial pressure by about 40 ppm in the surface seawater at Papa is caused by dissolved inorganic carbon consumption during primary production (Hamme et al., 2010). Figure 8 shows the measured partial pressure of surface seawater ( $p\text{CO}_{2,\text{SW}}$ ) during summer and autumn

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2007 and 2008 together with model simulation results with iron deposition in August 2008. During 2007 measured  $p\text{CO}_{2,\text{SW}}$  decreases slightly from July until October. In 2008 measured  $p\text{CO}_{2,\text{SW}}$  starts to decrease already in late July followed by a further sudden decline mid of August. We associate the latter with iron supply from Kasatochi ash. With iron deposition in August, a considerable decrease of  $p\text{CO}_{2,\text{SW}}$  is determined by the model which is in good agreement with the measurements, although modelled  $\text{CO}_2$  concentration decrease later and the model shows an offset of about  $25 \mu\text{atm}$ . Further discussion of potential reasons for the differences is presented in Sect. 5.

Altogether ECOHAM model results show that volcanic ash can stimulate algae blooms in surface ocean waters in HNLC regions of the NE Pacific Ocean. Soluble iron released from volcanic ash reacts as a key micronutrient for phytoplankton growth.

## 5 Model sensitivity studies and discussions

Two kinds of sensitivity studies were carried out to investigate the influence of (a) different supply dates of iron to the ocean and (b) varying amounts of volcanic ash and associated bio-available iron deposition into the ocean.

### 5.1 Timing

This sensitivity study aims to illuminate the influence of the supply date of iron to the ocean on phytoplankton growth. Therefore the same amount of iron as in the standard experiment is deposited during the same number of days as in the standard experiment, but instead of August, in different month (Fig. 9). As expected, phytoplankton concentration in the surface ocean reacts negligible on iron supply during the months of November to March as during wintertime the availability of sunlight represents the major limiting factor for phytoplankton growth. During April, May and June an increase in the spring bloom occurs, whereas iron supply during the summer months (June–September) generates an additional phytoplankton bloom of similar magnitude as the

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spring bloom. This sensitivity study emphasises the ability of the NE Pacific Ocean to form considerable phytoplankton blooms in the open ocean during the summer months upon iron supply. It demonstrates that external iron supply to the open NE Pacific, in particular from volcanic eruptions, may stimulate also zooplankton growth – a food source for salmon – and thus salmon survival rates in their critical last two years phase of their four year life cycle in the open ocean. Comparing sockeye salmon return runs to the Fraser river over the last century (Jones, 2010) with volcanic eruptions in this region illustrates that at least two other volcanic eruptions may be connected to increased salmon returns runs: Katmai in 1912 and Benzymianny in 1956.

## 5.2 Amount of volcanic ash and associated bio-available iron deposition into the ocean

Leaching experiments reveal a large variability in the release rate of iron from volcanic ash surfaces (Olgun et al., 2011). Only a few samples of Kasatochi ash are available showing lower iron release rates as assumed in our standard experiment (Olgun et al., 2012; Wang et al., 2010). As these samples consist of rather coarse ash, collected on a ship only about 13 km southwest of Kasatochi (Waythomas et al., 2010), the iron release rate might be not totally representative, as smaller ash particles with larger surface area may carry larger amounts of bio-available iron. Another uncertainty is related to the deposition fluxes of volcanic ash to the ocean determined by dispersion and deposition modelling (Langmann et al., 2010b). Generally, volcanic ash dispersion and deposition models need a realistic characterisation of the ash source term of a volcanic eruption, e.g. erupted mass flux, ash cloud top height, vertical distribution of mass, ash particle size distribution and information of the temporal development of these quantities during an eruption. All these information are only partly available. In addition, atmospheric ash removal processes like gravitational settling, wet deposition and aggregation processes are not well constrained (e.g. Bonadonna and Folch, 2011), so that the end-product, the modelled removal fluxes of volcanic ash at the station Papa are subject of considerable uncertainty.

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To investigate these uncertainties, we conducted a number of sensitivity studies with different iron supply fluxes to the ocean (Fig. 10). The ocean biogeochemistry is able to consume more CO<sub>2</sub> (maximum drawdown 80 μatm) and to produce more phytoplankton when more iron is supplied than in the standard experiment. The more iron is supplied to the ocean, the faster is the CO<sub>2</sub> decrease in surface seawater after fertilisation. Macronutrients like nitrate, phosphate and silicate limit further CO<sub>2</sub> consumption when the iron supply rate is increased by a factor of more than 30. In addition, the ocean mixed layer depth in the NE Pacific Ocean is restricted to 20–40 m during summer (Whitney and Freeland, 1999) so that the volume of water to be fertilised is a factor of 2.5–5 smaller than e.g. in the Southern Ocean (MLD ~ 100 m). Therefore, stronger phytoplankton blooms might be expected in the southern hemispheric summer in the Southern Ocean after iron supply by e.g. volcanic eruptions. When an iron supply rate higher than a factor 30 compared to the standard experiment is chosen in the sensitivity study (Fig. 10), the modelled CO<sub>2</sub> partial pressure in surface seawater resembles the measured one best during the months after the fertilisation. To analyse if this is an effect of the one-dimensional column model simulation, further studies with three-dimensional ocean biogeochemical models will be necessary, which in contrast to the one-dimensional column model simulations presented here take into account horizontal advection and diffusion processes.

## 6 Conclusions and outlook

The first evidence of large scale volcanic iron fertilisation of the surface ocean came from MODIS satellite data of chlorophyll-*a* after the eruption of Kasatochi in August 2008 (Langmann et al., 2010a). Meanwhile in-situ measurements are available to confirm the presence of the unusual large-scale phytoplankton bloom in the NE Pacific starting in August 2008 and persisting until about October 2008 (Hamme et al., 2010). The current study presents the first ocean biogeochemical model study of this event providing further insight into the nutrient, phytoplankton and zooplankton situation of

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the NE Pacific Ocean after fertilisation by soluble iron attached to volcanic ash. Increased zooplankton concentration after the iron fertilisation by volcanic ash in late summer 2008 underpins the speculations of Jones (2010) of increased survival rates of sockeye salmon in 2008 leading to record return runs to the Fraser river in 2010.

5 Sockeye salmon migrate into the open ocean in their second year of life. The model simulations presented here demonstrate that optimal feeding conditions in this critical life stage were offered.

Further studies on the amount of ash and iron deposited into the ocean after the eruption of Kasatochi as well as the assumed oceanic physical and biogeochemical conditions will be necessary to fully evaluate the presented model results. Therefore, three-dimensional model simulations on multi-year time scales are planned to further illuminate the fertilisation impact on atmospheric CO<sub>2</sub> concentration by also analysing the biogeochemical processes in the deeper ocean.

To increase our current understanding of the volcanic ash fertilisation potential of the surface ocean, further progress of the iron processing in volcanic plumes and during long-range transport is necessary via modelling studies, field and laboratory measurements. Until now it is not well understood under which conditions the formation of bio-available iron on volcanic ash surfaces is supported (Ayris and Delmelle, 2012). Leaching experiments of volcanic ash reveal a large variability in the release rate of bio-available iron from volcanic ashes e.g. Olgun et al. (2011), emphasising the need for classifications e.g. according to the magma solid and gas composition and eruption conditions to better understand the impact of past and future volcanic eruptions on marine primary productivity and atmospheric CO<sub>2</sub>. It would be also wishful to assess the oceanic iron-fertilisation potential of volcanic ash for historical eruptions depending on the geographical volcano location, volcanic ash amount, macronutrient and micronutrient availability in the adjacent ocean areas and atmospheric conditions.

Although volcanic ash leaching experiments showed a large variability of the release rate of bio-available iron, they showed that iron bio-availability from volcanic ash surfaces is in the same range of that from mineral dust. Future studies should consider

volcanic ash versus mineral dust ocean fertilisation and associated climate impacts, as the amount of volcanic ash and bio-available iron attached to the ash surface deposited into the ocean during episodic large volcanic eruptions may exceed the annual dust flux by far. Gaiero et al. (2003) estimates that the iron deposition of the August 12 to 15 Mount Hudson's volcanic eruption in Chile in 1991 is equivalent to ~ 500 yr of Patagonian iron dust fallout. In addition, fresh volcanic ash can be re-mobilised from tephra deposits, in particular in dry regions. Wilson et al. (2011), for example reports such post-eruption volcanic ash clouds after the eruption of Mount Hudson in Chile being transported over the Patagonian desert for several months after the eruption occurred. The ocean iron fertilisation potential by such re-mobilised ash clouds remains to be analysed.

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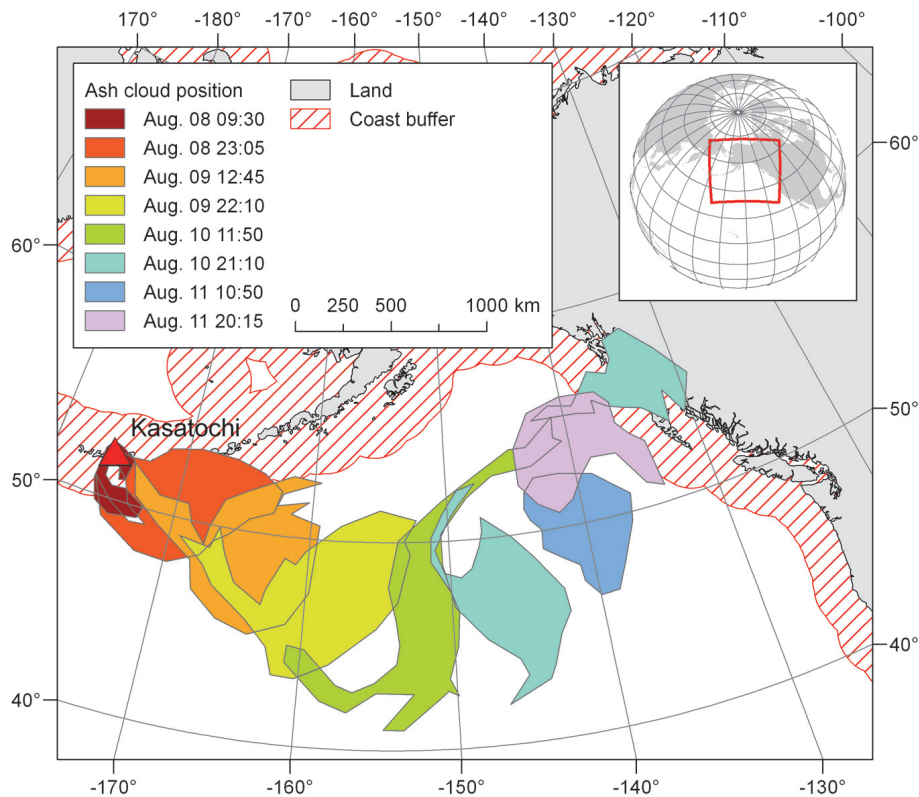
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**Fig. 1.** Atmospheric dispersion of the Kasatochi ash cloud from 8 August to 11 August 2008 (from Langmann et al., 2010a).

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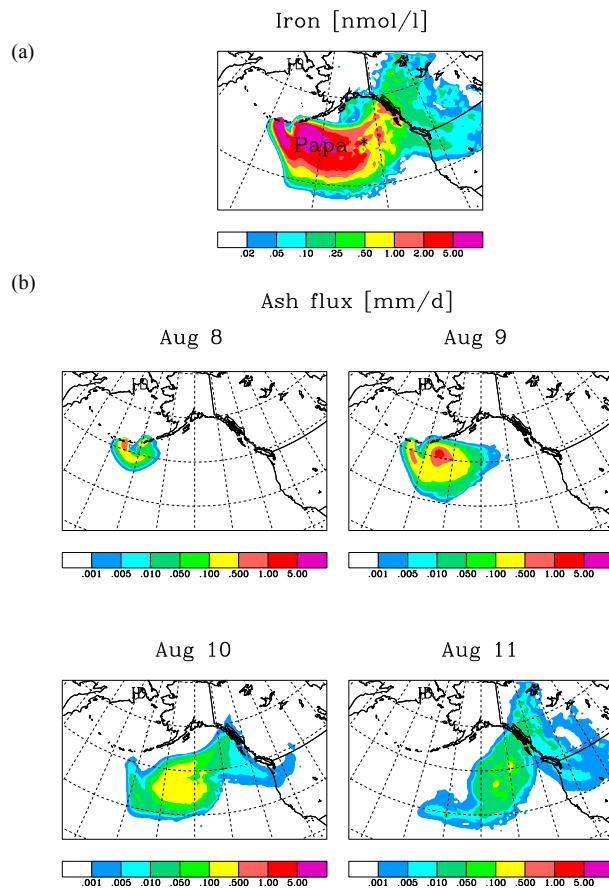
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**Fig. 2.** (a) Modelled maximum available ocean mixed layer iron concentration after the eruption of Kasatochi in the NE Pacific Ocean from 8–15 August 2008 ( $\text{nmol l}^{-1}$ ) and (b) modelled daily fluxes of volcanic ash to the NE Pacific Ocean ( $\text{mm d}^{-1}$ ). The location of station Papa is indicated in (a).

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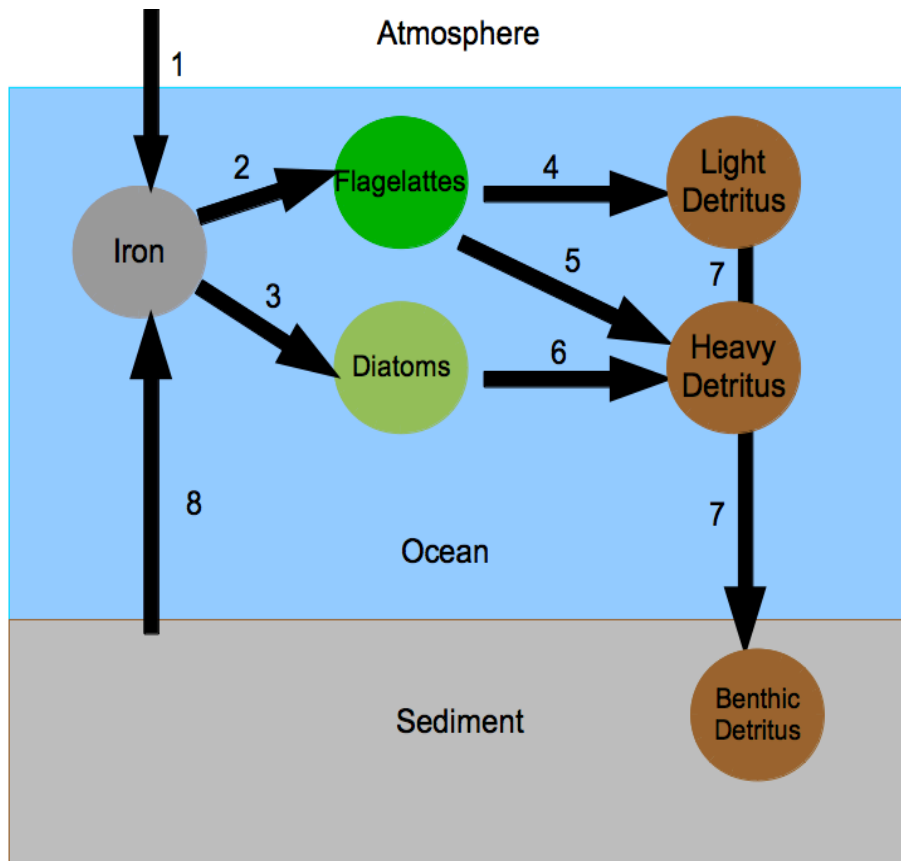
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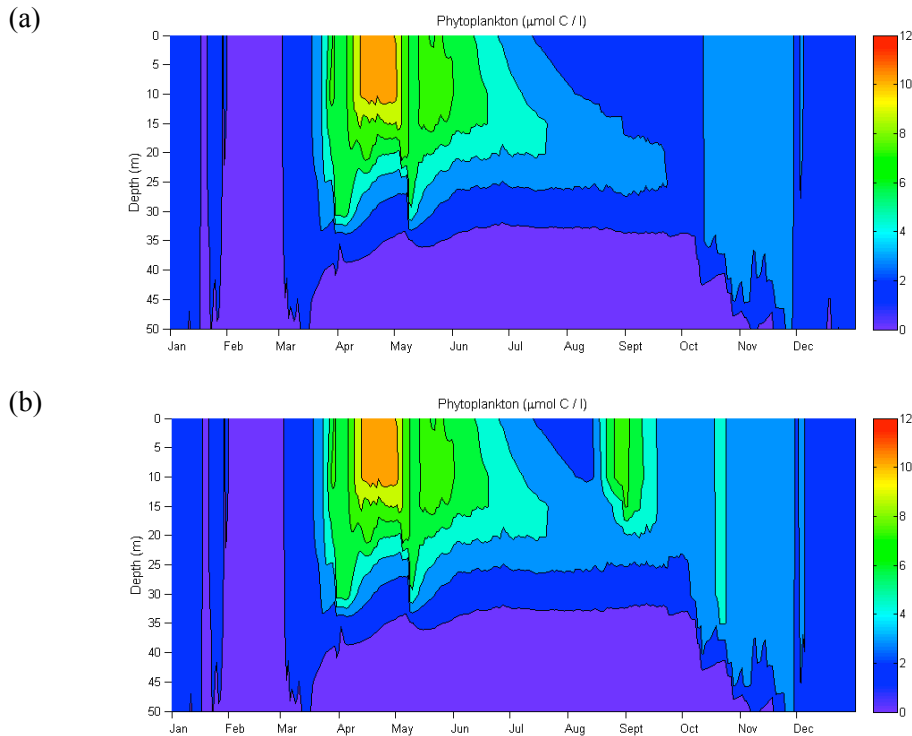
**Fig. 3.** Iron cycle in ECOHAM: (1) atmospheric iron deposition, (2) consumption of iron by flagellates, (3) consumption of iron by diatoms, (4, 5, 6) mortality and egestion, (7) sinking of detritus in the water column, (8) dissolution of iron from the sediment.

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**Fig. 4.** Temporal evolution of the vertical profile of phytoplankton in ( $\mu\text{mol C l}^{-1}$ ) in the upper 50m of the surface ocean at Papa during 2008 **(a)** without and **(b)** with iron fertilisation in August 2008.

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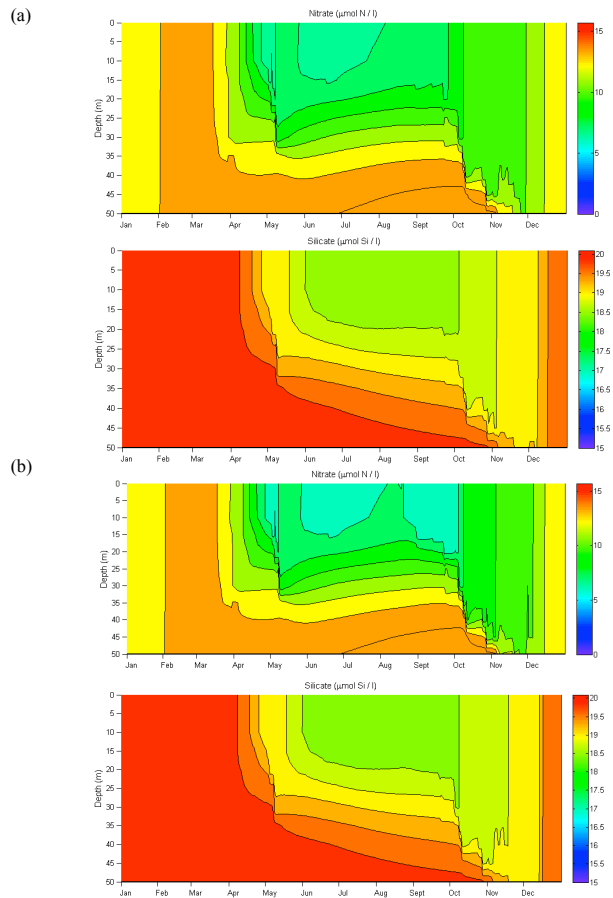
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**Fig. 5.** Temporal evolution of the vertical profile of nitrate ( $\mu\text{mol N l}^{-1}$ ) and silicate ( $\mu\text{mol Si l}^{-1}$ ) in the upper 50 m of the surface ocean at Papa during 2008 **(a)** without and **(b)** with iron fertilisation in August 2008.

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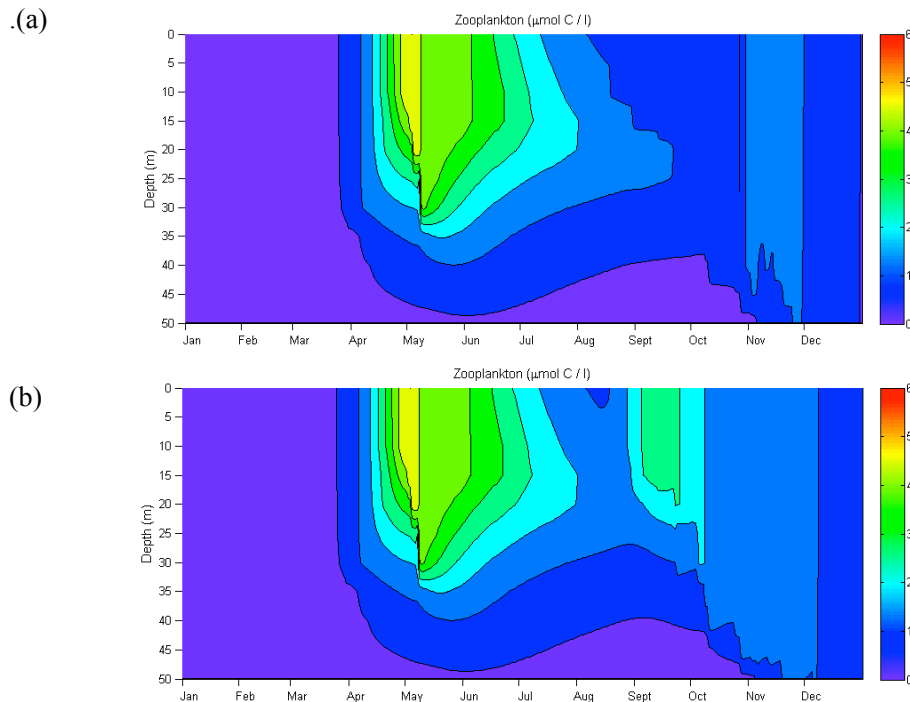
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**Fig. 6.** Temporal evolution of the vertical profile of zooplankton biomass ( $\mu\text{mol C l}^{-1}$ ) in the upper 50 m of the surface ocean at Papa during 2008 **(a)** without and **(b)** with iron fertilisation in August 2008.

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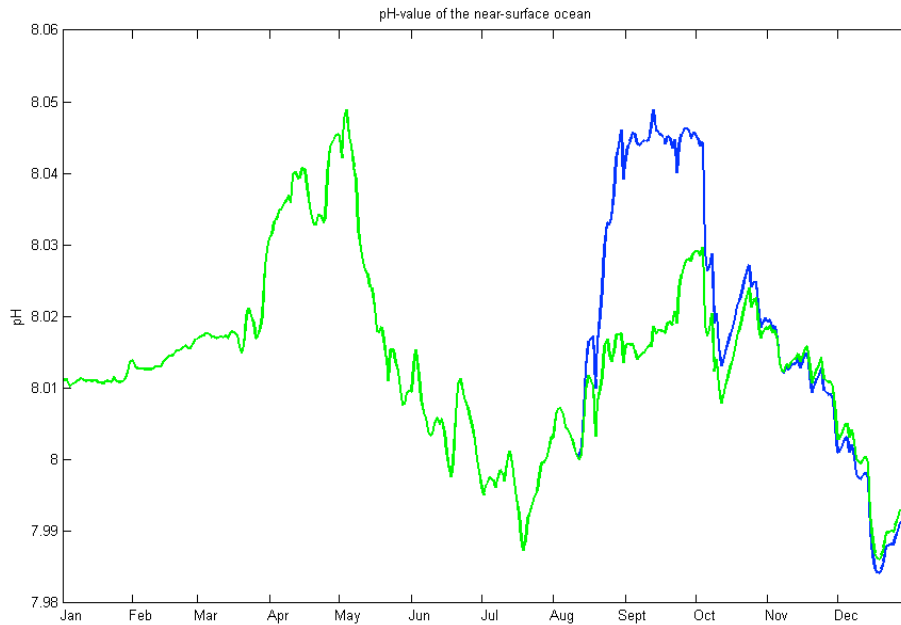
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**Fig. 7.** : Simulated pH without (green) and with Fe (blue) deposition in August 2008 at Papa.

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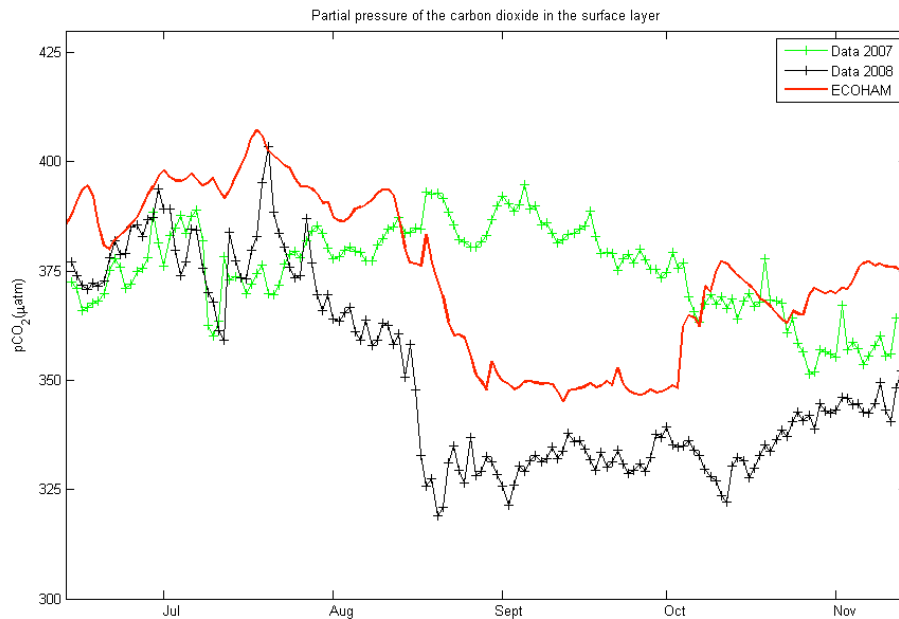
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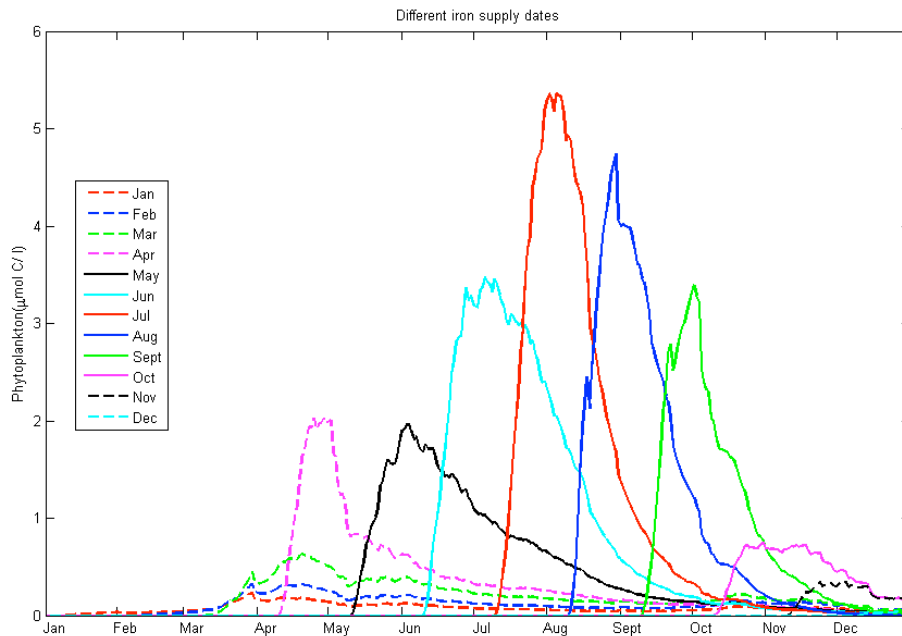
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**Fig. 8.** Measured and simulated  $p\text{CO}_{2,\text{SW}}$  in surface seawater at Papa. Measurements are shown for the year 2007 (green) and 2008 (black). Model results represent the year 2008 considering iron deposition with volcanic ash fall.

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**Fig. 9.** Modelled increase in phytoplankton concentration at Papa with different iron supply dates.

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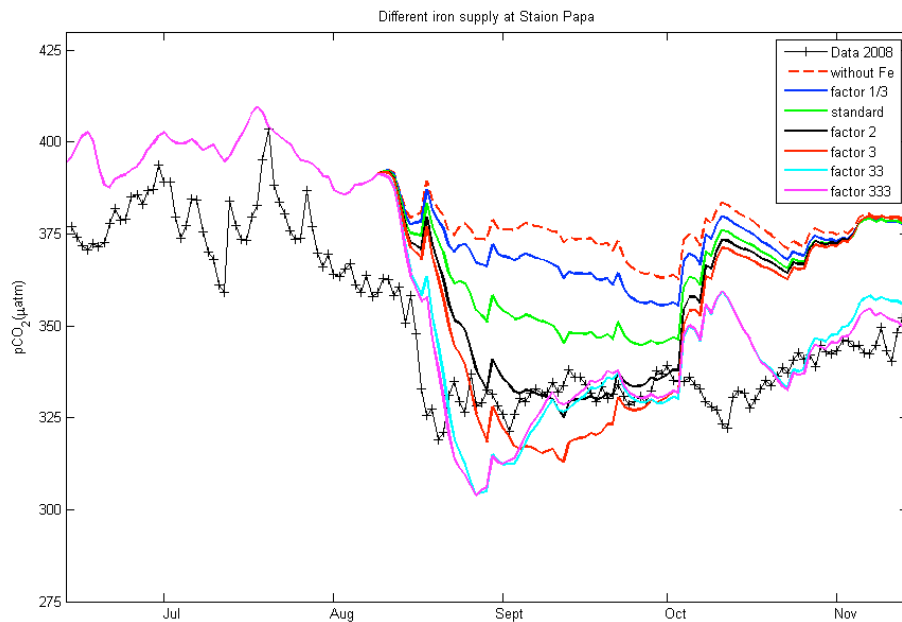
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**Fig. 10.** Modelled  $p\text{CO}_{2,\text{SW}}$  at Papa with different iron supply rates.

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