#### Answers to comments of anonymous referee #1:

#### Major issues:

This model fails to represent the basic seasonal cycle at station Papa. It shows a distinct and large spring bloom, while the main feature of the subarctic NE Pacific is in absence of a spring phytoplankton bloom. Chlorophyll at Station Papa has been shown to be low all year long with occasional, brief blooms at any time of year. See for example the early surface chlorophyll measurements presented by Parslaw (PhD thesis 1981) and reprinted in Boyd et al. (Global Biogeochem. Cycles 1998). Also, Whitney and Freeland (Deep-Sea Research II 1999) present nutrient cycles at Station Papa that show a fairly steady decrease in surface nitrate from March to September, in contrast to the sharper nitrate drawdown in spring in this model. Only silicic acid has a sharp decrease in about May through July. The authors state that macronutrient mixed layer concentrations stay at a constant level during summer in this location, but this is not true. While I sympathize with the authors' desire to avoid a full evaluation of the biogeochemical model results in this paper, the model has to at least reproduce the most important feature of the annual cycle in this region for other results from it to be believable. Two possible issues seem likely. First, the model may fail to represent iron concentrations or uptake kinetics properly (see next paragraph). Second, zooplankton in the model may not be exerting enough grazing pressure on the small phytoplankton whose growth is less limited by low iron concentrations. In this region, small zooplankton reproduce quickly to keep populations of small phytoplankton in check.

First, we would like to thank the reviewer for his/her constructive comments. We rechecked the model set-up carefully and could identify a number of overseen shortcomings in comparison with climatological data given by Whitney and Freeland (1999). By adapting the prescribed values for surface temperature, salinity and vertical mixing according to Whitney and Freeland (1999) for the water column at Papa, a substantial improvement in the reproduction of the annual phytoplankton cycle could be achieved. To avoid too strong jumps between the months, the prescribed monthly mixed layer depths based on Whitney and Freeland (1999) was overlain by a short period sinusoidal "noise" with an amplitude of 10 m. During the last 15 days of the year the mixed layer depth was enlarged by 60 m to a total depth of 170 m in order to introduce nutrients from below. Based on Gregg et al. (2003), a background atmospheric deposition flux of 3 nmol Fe m<sup>-2</sup> d<sup>-1</sup> has been added to the model (see Fig. 1 for more details of the iron budget), because in the applied 1-D model set-up the iron concentration in the column would be too much depleted without it. For more details of the iron budget see Fig. 1. The instantaneous release of iron from volcanic ash adds up to 7000 nmol Fe m<sup>-2</sup> and thus exceeds the daily background flux by a factor of more than 2000. The temporal cumulative iron budget of the first level (0 - 10 m) (see Fig. 1) shows the atmospheric deposition resulting in  $10.9 \times 10^3$  nmol Fe m<sup>-2</sup> y<sup>-1</sup>. From this amount the volcano eruption provided 7.0 \times 10^3 nmol Fe m<sup>-2</sup> y<sup>-1</sup>. The maximum amount of iron in the upper level was 1.2 nmol Fe/I (Fig. 2).

The maximum growth rate of flagellates has been defined as 0.8 d<sup>-1</sup>, the grazing pressure of microzooplankton on flagellates has been increased by enlarging the

maximum ingestion rate from  $0.5 d^{-1}$  to  $1.2 d^{-1}$ . In order to damp growth during the cold seasons the Q10-value of diatoms, determining the temperature dependency of the uptake has been enlarged from 1.5 to 3.0 (Berges et al., 2002). This factor determines the factor by which growth increases for every 10-degree rise in temperature. The C:Fe ratio (=400.000) in phytoplankton is now defined according to Cassar et al. (2007). We included a short description of the necessary prescribed values and biogeochemical constants in section 3 (Ocean biogeochemical model description) and the set of equations concerning the iron dynamics is given in the appendix of the revised manuscript as also requested by reviewer #2.



### Fig. 1 Temporal cumulative iron budget (0-10 m) at Papa with iron fertilisation in August 2008.

"Fe": iron amount, and the temporal cumulative fluxes: "mixing": vertical mixing; "diatoms": uptake by diatoms; "flagell": uptake by non-diatoms; "atmosph": atmospheric input due to dust deposition and ash deposition. Due to the small value of 0.96x10<sup>-3</sup> mmol Fe m<sup>-2</sup> yr<sup>-1</sup> the pelagic remineralisation flux is not shown

The new model set-up can reproduce the absence of the spring bloom. The model shows highest production rates in August when the mixed layer depth is smallest (Whitney and Freeland, 1999). The new figures show results of the second of two consecutively simulated years. For all cases the simulation of the first year was started with an iron concentration of 0.07 nmol Fe / I in the upper 150 m without considering fertilisation by volcano ash.



Fig. 2 Temporal evolution of the vertical profile of (a,b) total phytoplankton, (c,d) diatoms, (e,f) non-diatoms (μmol C / I) in the upper 63 m of the surface ocean at Papa during 2008 (a,c,e) without and (b,d,f) with iron fertilisation in August 2008 by the eruption of Kasatochi volcano.

We would also like to note, that Figures 3-10 of the original manuscript have been revised as well. To comment the reviewers comment on the annual cycle of nitrate and silicate at Papa, the revised data in the first 10 m of the surface ocean is shown below together with that of Whitney and Freeland (1999). With the revised model set-up, the modelled annual cycle of nitrate and silicate now satisfactory resembles the measurements, although silicate reaches the annual minimum with a delay of about two months. The exact values and the timing of the climatologic data could not be fully reproduced for the situation in 2008.



Fig. 3 Annual cycle of surface nitrate and silicate for the reference run 2008 without iron fertilisation in August.

The paper should present the modeled iron cycle as it does for the other nutrients. In particular, the initial iron concentration of 0.2 nmol Fe L-1 is about three times too large for this region (see Johnson et al., Deep-Sea Res. II, 2005). Also, more details are required regarding mixing rates at the base of the mixed layer (is iron being transported upward at too fast a rate?) and whether there is some other source of iron in the model / whether it is restored to some set value. The model assumes that all dissolved iron in the surface is bioavailable, while many studies have shown it is not. This might be okay, because the iron uptake kinetics used appears to be scaled to dissolved iron not soluble iron, but the authors should clarify.

### In addition to Fig. 1 above, the annual cycle of iron is shown below:





Fig. 4 Temporal evolution of the modelled vertical profile of dissolved iron in [nmol Fe/l] in the upper 63 m of the surface ocean at Papa during 2008 (a) without and (b) with iron fertilisation in August 2008.

By adapting the revised model set-up (see description above), the iron concentrations fit the observations much better now.

Mixing rate at the base of the mixed layer: The vertical diffusion coefficients below the mixed layer are set to  $0.134 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup> in the model set-up. They gradually increase in the mixed layer, until a maximum value of 0.028 m<sup>2</sup> s<sup>-1</sup> is reached close to the surface. The resulting annual upward flux of iron across the 30 m depth line was  $0.71 \times 10^{-2}$  mmol Fe m<sup>-2</sup> yr<sup>-1</sup> for the reference run which is about the double of the annual atmospheric background flux ( $0.37 \times 10^{-2}$  Fe mmol m<sup>-2</sup> yr<sup>-1</sup>). We clarified this issue in the revised manuscript accordingly.

Other sources of iron in the model: As illustrated in Fig. 3 of the original manuscript and written in section 3, one source of iron is the dissolution of iron from the sediments. However, for the one-year cycle investigated in the manuscript, this does not play a role at the location of Papa in the NE Pacific Ocean, with an approximate ocean depth of 4250 m. For the pelagic system remineralisation of iron is implemented. For the reference run it results in  $0.71 \times 10^{-3}$  mmol Fe m<sup>-2</sup> yr<sup>-1</sup> in the upper 10 m. By including the wording 'dissolved', when introducing the initialisation of iron in the model in section 3 as well in Fig. 4 above, we note that we model the dissolved and bio-available iron cycle, so that a necessary clarification proposed by the reviewer has been addressed. In addition, we added supplementary material (appendix) describing the iron cycle in detail, as this has been requested by reviewer 2 as well.

The inappropriate presence of a spring bloom in the model also affects the timing sensitivity studies. The authors show that the modeled ecosystem does not respond as strongly to volcanic ash input during the spring as during the late summer, presumably because there is already a bloom going on in the spring. However, in the real subarctic NE Pacific that lacks a spring bloom, the region seems likely to respond as strongly in the spring as late summer.

As already demonstrated above, the new model simulations with the revised set-up of the model could solve this problem. We now determine a stronger response of the biogeochemical system after the iron input released from volcanic ash (See above Fig. 2).

The paper makes a number of statements regarding the link between the Kasatochi eruption and record Fraser River salmon returns two years later that are not supported by data / analysis in this paper or cited research. I agree that the model results could be used to support enhanced zooplankton production from the eruption event, but the model (since it does not include salmon) provides no evidence that this could significantly increase salmon survival rates. No evidence is presented for the statement that two other eruptions can be connected to large salmon runs. The model also does not demonstrate that a relatively small additional zooplankton population in late summer represents optimal feeding conditions for salmon. A more appropriate citation for the Kasatochi salmon link than a Nature news article is Parsons and Whitney, Fish. Oceanogr. 21:5, 374–377, 2012.

We agree with the reviewer that the model can only demonstrate enhanced zooplankton production after the eruption of Kasatochi. With the revised model setup the increase is even more pronounced (see Fig. 5 below), thereby pointing to optimal feeding conditions for salmon. This modelled increase in zooplankton represents an important indication for a potential connections between the Kasatochi eruption and record Fraser River salmon returns, which has not been presented before. But we agree with the reviewer that everything beyond this remains speculative, as also the hypothesis and discussion in Parsons and Whitney (2012). The nature news article citation is replaced by that of Parsons and Whitney





Fig. 5. Temporal evolution of the modelled vertical profile of zooplankton biomass in  $[\mu mol C / I]$  in the upper 63 m of the surface ocean at Papa during 2008 (a) without and (b) with iron fertilisation in August 2008.

Concerning the reviewers comment that no evidence is presented for the statement that two other eruptions can be connected to large salmon runs, we realised that we cited the wrong article. The citation of Jones (2010) is replaced by Larkin, K., Canada sees shock salmon glut, Nature News, available at

http://www.nature.com/news/2010/100903/full/news.2010.449.html, doi:10.1038/news.2010.449, (2010) in the revised manuscript. The article contains a figure on Fraser River sockeye salmon return runs (see Fig. 6 below). It presents the missing evidence in the original manuscript on the connections of 20 million sockeye salmons which returned to the Fraser River in 1958 and the volcanic eruption of Benzymianny in 1956 (see also Parsons and Whitney, 2012) and the volcanic eruption of Katmai in 1912 and a sockeye return run of nearly 40 million sockeyes. The revised manuscript has been modified accordingly.



Fig. 6. Fraser river sockeye salmon return runs from 1890-2010. Figure copy from Larkin (2010).

### Moderate concerns:

The abstract does not summarize the results fully or make clear what new insights are presented in the paper. I suggest that the 2/3 of the abstract that summarizes the introduction be reduced and the portion of the abstract summarizing the results of the paper be expanded.

The abstract has been modified as proposed by the reviewer:

In High-Nutrient-Low-Chlorophyll regions, phytoplankton growth is limited by the availability of water-soluble iron. The eruption of Kasatochi volcano in August 2008 led to ash deposition into the iron-limited NE Pacific Ocean. Volcanic ash released iron upon contact with seawater and generated a massive phytoplankton bloom. 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 a phytoplankton bloom in the summer of 2008. Associated with this bloom, macronutrient concentrations such as nitrate and silicate decline and zooplankton biomass is enhanced in the ocean mixed layer. The simulated development of the drawdown of carbon dioxide and increase of pH in surface seawater is in good agreement with available observations. Sensitivity studies with different supply dates of iron to the ocean emphasise the favourable oceanic conditions in the NE Pacific in particular during July and August in comparison to other months to generate massive phytoplankton blooms. By varying the amount of volcanic ash and associated bio-available iron supplied to the ocean model results demonstrate that the NE Pacific Ocean has higher capabilities to

consume  $CO_2$  after iron fertilisation than those observed after the volcanic eruption of Kasatochi.

# Please expand on the comment at the end of section 3 that "comparing temporal and horizontal scales it appears appropriate to neglect horizontal (processes). . ." Station Papa is situated right in the geostrophic flow to the east, so horizontal processes are an important process there.

We agree with the reviewer that this issue needs clarification. The meteorological forcing data introduced on page 9237, lines 18-21 of the original manuscript have been interpolated to a 5°x5° latitude-longitude grid between 177.5-132.5°W and 40-60°N consisting of 10 x 4 grid cells, as the original purpose was to carry out 3-D model simulations. In this horizontal resolution, it appears appropriate to neglect the influence of the lateral boundaries and horizontal advection and diffusion, in particular as the focus of this study is on the summer months of 2008, where wind speed is considerably lower compared to the rest of the year (Whitney and Freeland, 1999), so that we decided to carry out 1-D column model simulations. Therefore, the results presented in the manuscript are representative for a 5°x5° area from 145-150°W and 47.5-52.5°N, including the location of the station Papa at the middle of the eastern edge. These additional explanations are now included in the revised manuscript.

### It's surprising that the volcanic ash run has nearly identical silicic acid concentrations to the no eruption run. The annual drawdown in silicic acid in the model is also much smaller than in the observations. Are the modeled diatoms not responding dramatically to the iron addition?

As already described above, the new model simulations with the revised set-up of the model solves this problem. We now determine an annual cycle of nitrate and silicate, which satisfactory resembles the measurements (see Fig. 3 above). Upon iron supply, the response in silicate is stronger now. To demonstrate the response in phytoplankton species, Figure 4 of the original manuscript has been extended to show also nanophytoplankton and diatoms (see Fig. 2 above).

# That the pCO2 drawdown is faster with larger iron additions is a pretty interesting result that is not well highlighted in the paper. One might have expected the bloom to become larger or last longer, but to start faster is cool. What about the model creates this situation? Does it arise from the iron uptake kinetics?

The new model simulations with the revised set-up of the model show a maximum deviation of marine surface pCO<sub>2</sub> of 35 µatm between the standard run and the run with fertilisation (Fig. 7a). The deviation between observed values in 2007 and 2008 is highest in August after the Kasatochi eruption ( $\Delta$ pCO2=70 µatm). A part of this deviation can be explained by the different years in which the deviation before the Kasatochi eruption was already 20 µatm. On the other hand the lower deviation and the slower decrease in the simulation after the eruption can be explained by the assumed climatologic mixed layer depth of 40 m in August which is about 2 times

larger than the situation in 2008 shows (http://www.pac.dfompo.gc.ca/science/oceans/data/projects/argo/MLD/Mld2784.gif ). The sensitivity runs with different amounts of iron deposition show that the maximum draw down of  $pCO_2$  can reach 75 µatm (Fig. 7b). The  $pCO_2$  drawdown is faster with larger iron additions. The speed of draw down is governed by the limitation factor of iron for diatoms: During days of strongest iron input in the normal fertilisation run this factor is about 0.5 (0.0 stands for total limitation, 1.0 corresponds with no limitation). In the fertilisation run with maximum iron input the factor is 0.99 which induces an increase of effective growth rate of about 200%.



Fig. 7 Modelled and observed marine  $pCO_2$  at Papa (a) with and without iron fertilisation in August 2008; (b) with different iron supply rates. The factors are related to the volcanic ash fertilisation run with factor=1 which equals 7 µmol m<sup>-2</sup>, iron input factor=1/3 equals 2.33 µmol m<sup>-2</sup>, factor=2 equals 14 µmol m<sup>-2</sup>, factor=3 equals 21 µmol m<sup>-2</sup>, factor=33 equals 231 µmol m<sup>-2</sup>, and

### factor =333 equals 2331 $\mu$ mol m<sup>-2</sup>.

The statement near the end of section 5.2 that a 30 times higher iron supply creates a modelled pCO2 that best resembles the measured one seems somewhat misleading.

The model begins with a much higher pCO2 than the observations, so it's really the total drawdown or change that should be compared rather than the final pCO2 value.

We agree with the reviewer, that this sentence is misleading and removed it from the manuscript.

### Minor comments:

Section 2 suggests an iron concentration at Station Papa resulting from the Kasatochi eruption of 1-2 nmol L-1, but Langmann et al. (2010b) estimate 0.3-0.7 nmol L-1. Please clarify the reason for the increased estimate.

By adapting the revised model set-up as described before, the amount of iron deposition necessary in the model to generate the observed marine  $pCO_2$  drawdown of about 50 µatm, is now in agreement with the estimate of Langmann et al. (2010b). This is corrected in the revised manuscript

## *End of section 2: One of the SERIES iron enrichment experiment papers might be a better reference here than Wells (2003), which reports on iron measurements during IronExII in the equatorial Pacific.*

According to the reviewer's suggestion, the reference to Wells (2003) is replaced by Boyd et al. (2004). In addition, the respective sentence in the revised manuscript is modified as follows: 'Results from mesoscale iron enrichment experiments in the NE Pacific (Boyd et al., 2004) show that an increase of surface ocean iron concentrations by 1–2 nmol/l is sufficient for large diatoms to grow rapidly in this iron-limited region.'

Given that the paper presents pCO2 and pH results, some brief details about the carbon cycle in the model might be appropriate. Does the ecosystem include calcification? What gas exchange parameterization and atmospheric pCO2 are used? What starting values of DIC and Alkalinity are used? Poor initial conditions or representation of some controlling processes may explain the higher model pCO2 than observed.

The simulation of the carbonate system is described in Lorkowski et al. (2012): "The model also simulates the production of calcium carbonate (CaCO3), but in a very simplified way: the flagellates produce calcite together with organic matter (OM), the corresponding molar production ratio is CaCO3:OM is 1:70. The carbonate shells become part of the fast sinking detritus and are dissolved while sinking through the water column. The dissolution rate is a function of the carbonate oversaturation. The air-sea flux of CO2 is calculated according to Wanninkhof (1992). The pCO2 in seawater is calculated from the water temperature, salinity, DIC and TA (Total Alkalinity) by applying the equilibrium equations of the carbonate system using the carbonic acid constants according to Mehrbach et al. (1973) as refit by Dickson and Millero (1987). The surface pCO2 is calculated in the upper layer of the model (Weiss, 1974)."

The initial condition of DIC and TA was 2100 and 2250  $\mu$ mol kg<sup>-1</sup>, respectively.

### In the pCO2 discussion at the end of section 4, the authors should cite and acknowledge the source of the pCO2 data.

pCO2 is available from: http://cdiac.ornl.gov/ftp/oceans/Moorings/Papa\_145W\_50N. A citation to Sabine et al. (2010) is added to the revised manuscript.

### References

Boyd, P. W., Law, C. S., Wong, C. S., Nojiri, Y., Tsuda, A., Levasseur, M., Takeda, S., Rivkin, R., Harrison, P. J., Strzepek, R., Gower, J., McKay, R. M., Abraham, E., Arychuk, M., Barwell-Clarke, J., Crawford, W., Crawford, D., Hale, M., Harada, K., Johnson, K., Kiyosawa, H., Kudo, I., Marchetti, A., Miller, W., Needoba, J., Nishioka, J., Ogawa, H., Page, J., Robert, M., Saito, H., Sastri, A., Sherry, N., Soutar, T., Sutherland, N., Taira, Y., Whitney, F., Wong, S.-K. E., and Yoshimura, T.: The decline and fate of an iron induced subarctic phytoplankton bloom, Nature, 428, 549–552, 2004.

Berges, J. A., Varela, D. E., and Harrison, P. J.: Effects of temperature on growth rate, cell composition and nitrogen metabolism in the marine diatom *Thalassiosira pseudonana* (Bacillariophyceae), Mar. Ecol. Progr. Ser., 225, 139–146, 2002.

Cassar, N., Bender, M. L., Barnett, B. A., Fan, S., Moxim, W. J., Levy II, H., and Tilbrook, B.: The Southern Ocean biological response to aeolian iron deposition, Science, 317, 1067–1070, doi:10.1126/science.1144602, 2007.

Dickson, A. G., and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Research, 34(10), 1733–1743, 1987.

Gregg, W. W., Ginoux, P., Schopf P. S., and Casey, N. W.: Phytoplankton and iron: validation of a global three-dimensional ocean biogeochemical model, Deep-Sea Research II, 50, 3143–3169, 2003.

Lorkowski, I., Pätsch, J., Moll, A., and Kühn, W.: Interannual variability of carbon fluxes in the North Sea from 1970 to 2006 - Competing effects of abiotic and biotic drivers on the gas-exchange of CO<sub>2</sub>, Estuarine, Coastal and Shelf Science, 100, 38–57 [doi:10.1016/j.ecss.2011.11.037], 2012.

Mehrbach, C., Culberson, C. H., Hawley, J. E., and Pytkowicz, R. M.: Measurement of apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnology and Oceanography, 18(6), 897–907, 1973.

Sabine, C., Maenner, S., and Sutton, A.: High-resolution ocean and atmosphere pCO2 time-series measurements from mooring Papa\_145W\_50N, http://cdiac.esd.ornl.gov/ftp/oceans/Moorings/Papa\_145W\_50N/. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.TSM\_Papa\_145W\_50N, 2010.

Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, J. Geophys. Res., 97 (C5), 7373–7382, 1992

Weiss, R. F.: Carbon Dioxide in Water and Seawater: The Solubility of Non-ideal Gas, Mar. Chemistry, 2, 203–215, 1974.

Whitney, F. A., and Freeland, H. J.: Variability in upper-ocean water properties in the NE Pacific Ocean, Deep-Sea Research II, 46, 2351–2370, 1999.