First of all, we thank the reviewers very much for their constructive comments and advices, which helped to improve the manuscript a lot. Please find our reply below. Best regards,

Tronje Kemena and co-authors

# Reviewers' comments:

# Reviewer #1:

This is an interesting paper describing potential future changes in marine phosphorus (P) cycling over the coming two millennia as obtained with an earth system model of intermediate complexity. The major conclusions are that there are large uncertainties in these projections due to our lack of knowledge of the expected changes in P supply due to weathering and benthic release. An interesting observation is that, in this model, nitrogen fixation cannot keep up with P supply. The paper is generally well-written and deserves rapid publication. I do have a number of recommendations that I suggest the authors consider in a revision:

1. The presentation of the scenarios could be improved. In the model, 12 different runs were performed to explore how the marine P cycle responds to different model settings. The differences in the results of these scenarios play a crucial role but it takes the reader quite some time to figure out what is what. This could be improved if the sequence of the 12 scenarios in the text would be the same as in Table 1. A brief explanation of the various groups of scenarios could also be added in the caption of figure 2. We changed the sequence in Table 1 to fit the description in section 2 (with exception for the simulation Anthr). The descriptions and sequence of the burial experiments were also improved. We start in section 2.3 (burial experiments) with a general description how sinking organic matter interacts with the subgrid bathymetry and than explain how benthic fluxes of P are calculated:

"The water column model is not coupled to a prognostic and vertically resolved sediment model. Instead, sinking organic matter interacts with the sediment via "transfer functions" (Wallmann, 2010) on a detailed subgrid bathymetry (Somes et al., 2013). Sinking organic matter is partially intercepted at the bottom of each grid box by a sediment layer and the intercepted amount depends linearly on the fractional coverage of the grid box by seafloor. The intercepted organic P is remineralized in accordance with Eq. (1) and Eq. (2), whereby organic C and N are completely remineralized under oxygen or nitrate utilization without any burial.

Fractional coverage of every ocean grid box by seafloor was calculated on each model depth level according to the subgrid bathymetry (Somes et al., 2013). The subgrid bathymetry was inferred from ETOPO2v2 (National Geophysical Data Center, 2006). ETOPO2v2 has a horizontal resolution of 2-minutes fine enough to adequately represent continental shelves and slopes. The coarse standard model bathymetry in the UVic model has a horizontal resolution of 1.8° latitude x 3.6° longitude." (Line 126-137)

We added also a brief description of the different groups of scenarios to the caption of Table 1: "We divided all simulations in four groups indicated by different colors. These are: reference simulations (in black) with and without anthropogenic fluxes of P; simulations with different formulations for the burial (in red beginning with the acronym Bur); simulations with weathering fluxes of P for different climate sensitivities (in blue beginning with the acronym Weath); and simulations with different representations of the sediment (in purple)."

# 2. The reasons for the N limitation upon ocean deoxygenation could be mentioned explicitly in the abstract.

We mention now the reasons for the N limitation already in the abstract:

"In the model, nitrogen fixation was not able to adjust the oceanic nitrogen inventory to the increasing P levels or to compensate for the nitrogen loss due to increased denitrification. This is because low temperatures and iron limitation inhibited the uptake of the extra P and growth by nitrogen fixers in polar and lower latitude regions."(Line 25)

3. It would be helpful to the reader to explicitly discuss the model assumptions leading to N limitation including uncertainties in changes in Fe cycling. I also would suggest to move Fig. S2 to the main paper. We mention and discuss in section 4.2 model assumptions for N uptake of diazotrophs and we mentioned how Fe limitation is simulated:

"In our model, diazotrophs are limited by P and Fe and are not limited by N. Their growth rate, which depends on temperature being zero below 15°C, is slower relative to non-fixing phytoplankton. These

characteristics allow them to succeed in warm, low-N and high-P environments that receive sufficient iron."(Line 362)

"We acknowledge that in the current study we did not account for potential future changes in iron concentrations (from atmospheric deposition, shelf inputs) and that the lack of a fully prognostic iron model may lead to a different sensitivity of the response of diazotrophs. Similarly we did not account for the ability of phytoplankton to adapt to changing N:P ratios, that may affect marine biological productivity and in turn deoxygenation. These would require further studies."(Line 374)

Further, we discussed how N-limitation and possible future changes in the Fe-cycle could affect the utilization of P by diazotrophs to section 5:

"As a next step it would be reasonable to investigate how different parameterizations of the N cycle and a full dynamic iron cycle will affect the utilization of the added P. For example benthic denitrification is not simulated in the UVic model. Model simulations showed for this century, that the enhanced denitrification in the water column could be compensated by less benthic denitrification (Landolfi et al., 2017), which could reduce the N-limitation and therefore enhance the effect of P fluxes on the biological pump. Sources of bioavailable Fe are still not well quantified and how these sources change under climate change is under debate (Hutchins et al., 2016; Mahowald et al., 2005). A more realistic representation of a dynamic iron cycle in UVic would affect N<sub>2</sub>-fixation in many areas of the global ocean (Fig. 8)." (Line 490)

We moved Fig. S2 to the manuscript and adapted the numbering.

# 4. There is a lot of recent work on river fluxes of P to the ocean that would be appropriate to reference for context.

We referenced to following publication in the text (Line 250, 234, 241):

- Harrison, J. A., Beusen, A. H., Fink, G., Tang, T., Strokal, M., Bouwman, A. F., Metson, G. S., and Vilmin, L.: Modeling phosphorus in rivers at the global scale: recent successes, remaining challenges, and near-term opportunities, Curr. Opin. Environ. Sustain., 36, 68–77, doi: 10.1016/j.cosust.2018.10.010, 2019.
- Beusen, A. H. W., Bouwman, A. F., Van Beek, L. P. H., Mogollón, J. M., and Middelburg, J. J.: Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum, Biogeosciences, 13, 2441–2451, doi: 10.5194/bg-13-2441-2016, 2016.
- Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., and Bouwman, A. F.: Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application, Global Biogeochem. Cycles, 19, 1–11, doi: 10.1029/2005GB002606, 2005.

Detailed comments (partly overlapping):

- Line 10: suggested change: ": : :.that enhanced weathering and increased benthic phosphorus (P) fluxes"

Added "that".

- Line 14 and 15 and elsewhere: "until the year 2300" Corrected.

- Line 25: suggested change: "In the model, nitrogen fixation was not able to adjust: : .": Added.

- Line 25. Here, it would help if the authors clarify why nitrogen fixation does not adjust to the high P levels. Because these are model results, this can be specified. We added a sentence to clarify this:

"This is because low temperatures and iron limitation inhibited the uptake of the extra P and growth by nitrogen fixers in polar and lower latitude regions."(Line 27)

- Line 27: "this contrasts with" Corrected.

- Line 27. Here, the authors could clarify whether the palaeo reconstructions refer to model studies or

reconstructions based on data or both and exactly how those results are different. We made here a very general statement, so we decided to remove this sentence.

- Line 49. Suggested change "the Earth has experienced" or "the Earth experienced" Corrected.

- Line 49. It's not clear what is meant by "climate OAE-like states". I would suggest to rephrase. We rephrased this sentence to be more specific:

"Evidence in the palaeo record indicates that the Earth has experienced several OAEs with large-scale anoxia, euxinia and mass extinctions (Kidder and Worsley, 2010)."(Line 51)

Line 66. What about increased inputs of Fe from continental shelves upon ocean deoxygenation?
 Could they alleviate the Fe limitation in the model? What is the uncertainty in the dust inputs?
 We just recognized that this sentence could imply that we simulate a dynamic dust cycle. Instead spatial dust limitation is based in UVic on present day observations. We decided to remove this sentence to not give this wrong impression.

- Line 79. "and improved representations of" Corrected.

- Line 96: "as the switching point" Corrected.

- Line 98: "so that" (instead of "such that") Corrected.

- Line 111 and Table 1: are benthic P fluxes equated to burial? I don't see the term benthic flux in Table 1. The terms need to be used consistently.

We refereed here to benthic P fluxes across the ocean-sediment boundary in general. To avoid confusion we replaced "benthic P fluxes" with "benthic P burial". In other text passages "benthic P fluxes" was replaced by "benthic P burial" or "benthic P release" respectively.

# - Line 112: in a print, the purple and blue are very difficult to differentiate

I am not sure, if you refer here to the color in Table 1 or to the general usage of purple and blue. However, we increased the color intensity of the purple in Table 1. We avoided using the combination of the colors green and red in all plots to improve the distinguishability of the colors for persons with green/red color blindness.

- Table 1: please add much more detail on the abbreviations in the text (or can you think of an easier notation?). Now it is very hard for the reader to keep the various model scenarios apart. Note that the sequence doesn't match the text and that the anthropogenic flux not quantified.

In brackets short expressions were added to let the reader easier identify how the abbreviations are related to changes in the model formulations:

*Bur\_res* (i.e. restricted release or P reservoir); *Bur\_Dun* (i.e. burial parameterization from Dunne et al. 2007); *Weath0.05*, *Weath0.10*, *Weath0.15*, *Weath0.38* (i.e. the number represents the preindustrial weathering flux); Anthr (anthropogenic)

For the model simulation *Anthr* we referred to Fig. 2, because we used a temporal variable weathering flux:

"The weathering flux in simulation Anthr is variable over time (Fig. 2a)." (Table 1)

- Line 136-138. Please explain this section on the organic C burial better: it seems contradictory that all organic C is remineralized but that there is still organic C burial.

We adapted the text to clarify that we calculate a 'virtual' C burial to determine the P burial. In this model no C burial is applied:

"Virtual is meant in the sense that there is no explicit burial of organic C in the model, and instead all organic C is remineralized in the deepest ocean layer. In this study we do not focus on changes in the C inventory and therefor  $BUR_c$  is just calculated to determine  $BEN_c$  in Eq. (2)." (Line 148)

- Line 258. "is essentially equal" Corrected.

- Lines 225-226. It is very well known already for a long time that total P in rivers can be mobilized in the

coastal zone and forms a key input of P to the coastal zone. These are not new findings of Benitez-Nelson, Compton et al. and Ruttenberg as suggested here, so I would suggest to rephrase this sentence.

We rephrased the sentence and added a reference to older studies:

"...(see Fig. 1, Benitez-Nelson, 2000; Compton et al., 2000; Ruttenberg, 2003). These studies give a range of total P fluxes to the oceans, which are higher than interfered from dissolved inorganic P fluxes shown already in previous studies (e.g. Martin and Meybeck, 1979; Rao and Berner, 1993)..." (Line 229)

- Same section: you could consider including a reference to the weathering & anthropogenic flux of P calculated from the Global News models (see the work of Seitzinger et al. 2010; Global Biogeochemical Cycles) and follow-up studies (e.g. Beusen et al. 2016; Biogeosciences) We cited in this paragraph Seitzinger et al. (2005) to reference to the Global News model.

- Lines 258. Change to "essentially" Corrected.

- Line 267. Change to "after the year" (note that "the" is missing before year in more places) Corrected.

- Line 327: Change to "a consequence" Corrected.

- Line 350. Change to "shown" Corrected.

- Line 358-359. This is an important piece of information that also should be given in the abstract, see comment above.

We added this information to the abstract.

"This is because low temperatures and iron limitation inhibited the uptake of the extra P and growth by nitrogen fixers in polar and lower latitude regions."

- Don't start a sentence with "So that" Improved.

- Line 440-443. Needs rephrasing since benthic P release is known to be important in the coastal zone from both experimental field studies and modeling.

Yes we agree with you. However, we focused here how a release of the **actual** inventory of sedimentary P could contribute to an increase in the oceanic P inventory. The deposition of fluvial particulate P to the sediment and its release was not simulated. We rephrased the text passage to state this more clear:

"This could imply that benthic release of P is actually negligible in comparison to the weathering fluxes of P, but the UVic model does not resolve coastal processes such as the deposition of reactive particulate P from rivers on the continental shelves and its dissolution and release to the water column. For a more honest comparison of benthic and fluvial P fluxes, a more detailed representation of coastal processes would be necessary to simulate deposition and release of fluvial P from the sediments at the shelf. However, we can conclude that the actual local inventories of P are too small to sustain a positive benthic P feedback over several millennial."(Line 457)

# - Line 459. The term "palaeo study" is vague. Please provide more information i.e. on the type of setting and time period.

We provided more informations to the palaeo study in the text:

"In the time period of the OAE1a and the OAE2, a substantial increase in  $N_2$ -fixation was also inferred from measurements of sediment nitrogen isotope compositions typical for newly fixed nitrogen conditions and from high abundances of cyanobacteria indicated by a high 2-methylhopanoid index (Kuypers et al., 2004)."(Line 481)

- Line 460. "not able to compensate: : :." Unless you are underestimating the Fe input to the ocean. A few lines on the uncertainties there (e.g. shelf Fe input, dustfield) would be useful. We added a discussion in the result and discussion section: Section 4.2:

"We acknowledge that in the current study we did not account for potential future changes in iron concentrations (from atmospheric deposition, shelf inputs) and that the lack of a fully prognostic iron model may lead to a different sensitivity of the response of diazotrophs." (Line 374) Discussion:

"Sources of bioavailable Fe are still not well quantified and how these sources change under climate change is under debate (Hutchins et al., 2016; Mahowald et al., 2005). A more realistic representation of a dynamic iron cycle in UVic would affect  $N_2$ -fixation in many areas of the global ocean (Fig. 8)."(Line 495)

- 'line 480. Could be changed to "on benthic P fluxes in this model is eventually: : :" These results really depend on how the N and Fe cycles are parameterized – should be discussed in a few more sentences in the main text.

We added a short paragraph to section 5 and section 4.2 to discuss this (see also the last comment related to the Fe cycle):

# Section 4.2:

"In our model, diazotrophs are limited by P and Fe and are not limited by N. Their growth rate, which depends on temperature being zero below 15°C, is slower relative to non-fixing phytoplankton. These characteristics allow them to succeed in warm, low-N and high–P environments that receive sufficient iron."(Line 362)

"Similarly we did not account for the ability of phytoplankton to adapt to changing N:P ratios, that may affect marine biological productivity and in turn deoxygenation. These would require further studies." (Line 377)

# Discussion:

"As a next step it would be reasonable to investigate how different parameterizations of the N cycle and a full dynamic iron cycle will affect the utilization of the added P. For example benthic denitrification is not simulated in the UVic model. Model simulations showed for this century, that the enhanced denitrification in the water column could be compensated by less benthic denitrification (Landolfi et al., 2017), which could reduce the N-limitation and therefore enhance the effect of P fluxes on the biological pump."(Line 490)

# - Fig. S2: I would suggest to move this figure to the main paper.

We moved Fig. S2 to the manuscript and adapted the numbering.

# Reviewer #2:

Kemena et al. present 12 long-term global warming simulations of the UVic Earth System Model of Intermediate Complexity to assess how projected P and O2 inventories depend on implemented weathering and sedimentary fluxes. The focus is on biogeochemical feedbacks, as the physical response is almost identical across the simulations. They suggest weathering fluxes contribute most to projected increased P inventories. I consider this to be a welcome contribution to the field of long-term Earth system projections. I have several questions regarding the methodological approach and conclusions which should be considered to improve the readability and focus of the manuscript.

-Bur simulations: I find it hard to judge the "meaningfulness" of the Bur simulations given that they release P from an unlimited reservoir. The Bur\_Res simulation seems to indicate an upper limit on the potential P release, which all other Bur simulations appear to surpass. So all other simulations release more P than can be assumed to be in the sediments, correct? Should the reservoir constraint not apply to all simulations? You might want to consider disqualifying those simulations a bit faster in the text and highlight the importance of this constraint a bit clearer, including the abstract and method/results section.

In the Bur simulations, we investigate uncertainties in the release of P from the sediment in the future by analyzing different parameterizations for benthic P fluxes. These transferfunctions are used in various studies as a state of the art approach (e.g. Bohlen et al., 2012; Niemeyer et al., 2017; Wallmann, 2010), because transferfunctions are less cost intensive and easier to implement than full complex sediment models (Soetaert et al., 2000). In this study we like to push forward the development of these transferfunctions, but at the same time we like to point out how large uncertainties of such simple transferfunctions can be, therefore we believe that the results of all model simulations should be published.

- Wallmann K (2010) Phosphorus imbalance in the global ocean? Global Biogeochem Cycles 24:1–12. doi: 10.1029/2009GB003643
- Bohlen L, Dale AW, Wallmann K (2012) Simple transfer functions for calculating benthic fixed nitrogen losses and C:N:P regeneration ratios in global biogeochemical models. Global Biogeochem Cycles. doi: 10.1029/2011GB004198
- Niemeyer D, Kemena TP, Meissner KJ, Oschlies A (2017) A model study of warming-induced phosphorus–oxygen feedbacks in open-ocean oxygen minimum zones on millennial timescales. Earth Syst Dyn 8:357–367. doi: 10.5194/esd-8-357-2017
- Soetaert K, Middelburg JJ, Herman PMJ, Buis K (2000) On the coupling of benthic and pelagic biogeochemical models. Earth-Science Rev 51:173–201. doi: 10.1016/S0012-8252(00)00004-0

-Weathering simulations: Why do these simulations not have a burial formulation? Of course, addition of P to an otherwise "closed" ocean just increase its P inventory. Would it not be important to assess the feedbacks associated with deposition and redissolution in this context, as increased P supply to the upper ocean stimulates NPP, export and deposition? I could not find a discussion on this matter in the manuscript.

In these simulations just anomalies ( $W_P = W_{P,0} \cdot (f(NPP, SAT) - 1)$  with f(t = 0) = 1) for weathering were applied. In a future study we could imagine to investigate above mentioned possible negative feedbacks. However, all simulations show an increase in NPP, export and the herewith associated increase in burial of P can be seen in all Bur simulations, especially in simulation Bur\_high and Bur\_Res with net global P loss at the end of the simulation. However in this study the low N availability is the predominant process that prevents the ocean from further deoxygenation (and not high burial rates in P). This can also be found in model simulations where such a negative feedback could by P are possible (Niemyer et al., 2017).

Niemeyer D, Kemena TP, Meissner KJ, Oschlies A (2017) A model study of warming-induced phosphorus–oxygen feedbacks in open-ocean oxygen minimum zones on millennial timescales. Earth Syst Dyn 8:357–367. doi: 10.5194/esd-8-357-2017

-It is not clear to me which simulation corresponds to the best estimate reported in the abstract and conclusion. Do you just add the result of the Weath0.15, Bur\_Res and Anthr simulations? You may want to guide the reader a bit better here, and explain why these simulations are simply additive? That seems strange to me, as for instance, the Bur\_Res simulation would suggest a W0=0.41 TmolPa-1, much higher than the 0.15 TmolPa-1 considered in Weath0.15.

We added these values together for following reasons:

The anthropogenic input of P is prescribed and is extracted from Filippelli (2008). The weathering input depends on environmental parameters and parameters of the weathering equations. The environmental parameters are just affected by the climate and therefore the changes in atmospheric  $CO_2$  concentrations. In our simulations, the climate develops in all simulations almost in the same way, so this would not affect the addition. However, you are right the export is much higher for simulations with larger oceanic P inventories. We hope that the additional removal of P will not affect the oceanic P inventory too much on this timescales.

We shortly discussed your concerns in section 5:

"In this simple addition of the P inventories we cannot account for feedbacks, which would appear in a fully coupled model. For such high P inventories we would expect larger suboxia and therefore more P release from sediments and at the same time a stronger export of organic P that lead to increased P burial." (Line 471)

Filippelli GM (2008) The Global Phosphorus Cycle: Past, Present, and Future. Elements 4:89–95. doi: 10.2113/GSELEMENTS.4.2.89

-Language: I find the language at times ambiguous. Most importantly, the usage of benthic fluxes, burial and sediment release appear confusing, and it's not clear whether gross or net exchange is meant. Please consider explicitly introducing these terms and using them consistently.

To avoid confusion we replaced "benthic P fluxes" in by "benthic P burial" or "benthic P release" if possible. Benthic P burial and benthic P release is defined in section 2:

"P burial in the sediment  $(BUR_P)$  was determined in every grid box with sediment from the difference between the simulated detritus P rain rate to the sediment  $(RR_P)$  and the benthic release of dissolved inorganic P from the sediment  $(BEN_P)$ :

$$BUR_P = RR_P - BEN_P \tag{1}$$

where  $RR_P$  is the detritus flux from the ocean (in P units)." (Line 138)

We used these definitions consistently throughout the manuscript. P burial/release leads to a net loss/gain of P in the global P inventory. We are not sure what do you meant with "gross exchange". "Benthic fluxes of P" is used as a more general term and it describes fluxes of P across the benthic boundary layer.

-Balance between presentation of P and O2 response: Even though deoxygenation is mentioned in the title, there is very limited mentioning of deoxygenation in the abstract and discussion. The most important driver of ocean deoxygenation appear to still be circulation changes, and the assessed biogeochemical feedbacks should be presented in this context. There are several papers worth citing/discussing in the introduction and discussion on the matter of long-term projections of ocean deoxygenation, e.g.: Battaglia & Joss 2018, ESD, Yamamoto et al. 2015, GBC, Schmittner et al. 2008, GBC As such, the modeled circulation response may be compared to other long-term projections. The focus of this manuscript is to assess uncertainties in the projections of the P inventory and how this could affect deoxygenation. We agree that a reader of the title could expect a more general investigation of deoxygenation processes, therefore we decided to change the title of the manuscript to: "Ocean Phosphorus Inventory: Large Uncertainties in Future Projections on Millennial Timescales and its Consequences for Ocean Deoxygenation"

Furthermore deoxygenation is always analyzed in relation to changes in the P inventory as it was already mentioned in the introduction:

"Here, we build on this study and test the sensitivity of the marine P and  $O_2$  inventories in a climate change scenario on millennial timescales to different model formulations of P weathering and benthic fluxes." (Line 74)

We removed the sentence from section 3 to avoid the impression that just uncertainties in P land-ocean and P sediment-ocean fluxes can be the drivers for the large range of P fluxes:

"We found that the large range in P fluxes was not related to differences in the climate or atmospheric  $CO_2$  forcing, but rather to differences in parameterizations of P land-ocean (Sect. 3.1) and sediment-ocean (Sect. 3.2) interactions."

# Specific comments:

Line 27: "this is in contrast to paleo reconstructions": not clear what is meant from the text We made here a very general statement, so we decided to remove this sentence.

Line 29: "more reliable projections of ocean deoxygenation": context of ocean deoxygenation does not emerge from the abstract. How do the biogeochemical feedbacks assessed compare to uncertainties in circulation changes? Introduction: centers round CO2-driven ocean deoxygenation. Please include recent literature on ocean deoxygenation, and the fact that circulation changes are crucial for ocean deoxygenation associated with global warming, not CO2 per se.

We completely agree with you, circulation changes are crucial for ocean deoxygenation too, but there are a series of factors e.g. changes in oxygen solubility, stratification, wind and upwelling, respiration, circulation and mixing processes that effect deoxygenation (Levin, 2019; Oschlies et al., 2018). We added a sentence in the beginning of the introduction: "Many different processes affect the oxygen balance in the ocean (e.g. oxygen solubility, stratification, respiration, circulation, Levin, 2019; Oschlies et al., 2018)." We focus here on very long time scales and here we were not able to find an answer in literature to the question: "How do the biogeochemical feedbacks assessed compare to uncertainties in circulation changes?".

However, in this study we focus how uncertainties in benthic fluxes of P can affect the deoxygenation of the ocean and for this reason the temporal evolution of the ocean circulation is kept the same in all model simulations.

In one paragraph of the introduction we focused on  $CO_2$ , because the increase in atmospheric  $CO_2$  and consecutively climate warming is the most likeliest driver for OAEs. Actually changes in P supply (the same for circulation) are just a consequence of the  $CO_2$  induced global warming.

Levin LA (2018) Manifestation, Drivers, and Emergence of Open Ocean Deoxygenation. Ann Rev Mar Sci 10:229–260. doi: 10.1146/annurev-marine-121916-063359

Oschlies A, Brandt P, Stramma L, Schmidtko S (2018) Drivers and mechanisms of ocean deoxygenation. Nat Geosci 11:467–473. doi: 10.1038/s41561-018-0152-2

# Line 57: "could": will?

We replaced "could" with "will" as suggested.

2.3/2.4: Please consider presenting weathering first, consistent with presentation of results/Table 1

We changed the order of the experiments in Table 1 with first the burial experiments and than the weathering experiments to be more consistent with the order in the "Model and Methods" section.

# Line 126: "every grid box": every bottom grid box?

We clarified the text here, because in the sub grid bathymetry benthic fluxes are not just limited to the bottom grid box: "every grid box with sediment"

Line 137: "all organic C is remineralized in the deepest ocean layer": statement must be wrong? Eq. 3ac: potentially include z1000m on the respective lines for clarity. Eq. 4: Is there only a O2-feedback on P fluxes? Should the C burial/redissolution not also be O2-dependent? Potentially worthy of discussion. We adapted the text to clarify that we calculate a 'virtual' C burial to determine the P burial. In this model no C burial is applied:

"Virtual is meant in the sense that there is no explicit burial of organic C in the model, and instead all organic C is remineralized in the deepest ocean layer. In this study we do not focus on changes in the C inventory and therefor  $BUR_c$  is just calculated to determine  $BEN_c$  in Eq. (2)." (Line 148)

# Line 170: Please add numbers in parenthesis.

We clarified the text passage. The burial is by definition one magnitude larger see also Eq. 3b, c. Factor 0.14 and 0.014. We slightly rephrased the sentence:

"In the standard formulation, C burial is by definition one magnitude larger in slope and shelf regions compared to the deep ocean (see Eq. 3b, c)." (Line 168)

Line 183-200: Hard to understand. Examples below: We improved the paragraph as suggested (see below).

Line 187/188: "for the continental shelf and slope": how was this done for all other grid cells? We added a sentence to clraify this in the text:

"In accordance to Flögel et al. (2011), release of P from the deeper ocean (>1000 m) cannot exceed the rain rate of organic P to the sediment. For the continental shelf and slope,..." (Line 191)

# Line 194: "local inventory": what do you mean with this? Do all cells have this inventory? Or is this an upper limit for inventories globally?

Meant here is that 100% of the total solid P can be released. We rephrased the sentence and moved the introduction of  $RES_P$  to the next sentence. As the local inventory is given in  $\mu$  mol cm<sup>-2</sup> it scales also with increasing sediment coverage (for every grid cell with sediment coverage). 113  $\mu$  mol cm<sup>-2</sup> is the upper local inventory, we name it in the text now maximum local inventory ( $RES_{P,max}$ ):" Together, these assumptions convert to a maximum local inventory of total solid P in the active surface layer of  $RES_{P,max} = 113 \ \mu$ mol cm<sup>-2</sup> (Eq. 6a)." (Line 198)

Line 195/196: reservoir can be replenished, but excess P is permanently buried? Is the  $\Delta RESp$  the replenished P or excess P? Eq. 6: are the > and > correct?

Yes excess P is permanently buried. We replaced  $\Delta RES_P$  by  $\Delta RES_P/\Delta t$  to indicate that this is the change of RES<sub>P</sub> over time. The valid range of RES<sub>P</sub>, with 113  $\mu$  mol cm<sup>-2</sup> its upper limit, is defined in Eq. 6b.

# Line 197: "depending on environmental conditions": what do you mean with this statement? Depending how? Earlier you mentioned local inventories of 113 umol/cm2?

 $\text{RES}_{P}$  is the actual local P inventory and variable over time. During the spin-up simulation the local P inventories adapt to the environmental conditions like oxygen concentration or rain rate of P. I hope this is now clearer by introducing the maximum local inventory of P  $RES_{P,max}$  and the actual local inventory of P  $RES_{P}$ .

Line 277: "the way sediment P reservoirs are represented": if represented at all or not. 3.2: Preferably start section with PI RR (lines 295-299) and PI burial rates (lines 279- 283). Then, would strongly suggest changing the tone of this section, in that Bur simulations without a reservoir constraint are not realistic. Potentially exclude those runs from Figs.5-8, Figures are very busy anyway and lines are hard to tell apart. Or explain why those are considered for assessment of ocean deoxygenation, still. This question is answered in the comment (-Bur simulations) of the reviewer.

Line 308/309: Please add more citations of long-term O2 projections. We additionally cited Matear and Hirst (2003) as well as Shaffer et al. (2009). Line 374: "recovered": strange language. O2 inventory is still increasing and simulation has not reached steady state yet.

We replaced "recovered" with "reached present day values again"

# Line 377: How is AOU/O2sat calculated? Potentially discuss/mention Ito et al., 2004, GRL? We added a description how AOU/O2sat is calculated and discussed Ito et al., 2004:

"AOU is calculated from the difference between the  $O_2$  saturation concentration and the in situ oxygen concentration assuming that all ocean water leave the surface layer saturated in  $O_2$ . The calculation of AOU is in general biased to higher values, because in polar regions surface water leaves the surface water in respect to oxygen in a undersaturated state due to reduced air-sea gas transfer inhibited by sea ice (Ito et al., 2004). In UVic this leads to an overestimation of AOU by 30% (Duteil et al., 2013). For a warming ocean sea ice cover reduces which converts into an underestimation of the AOU anomaly in Fig. 9c." (Line 387-393)

Line 390: Are preformed nutrients carried as explicit tracers? Please introduce how signal is separated. We described the calculation of preformed nutrients in the figure caption of Fig. 10: "Preformed nutrients are calculated as the difference between remineralized and total nutrient content. The calculations assume that all ocean water leave the surface layer saturated in O<sub>2</sub>."

# Line 397: "are likely": how come you are not sure about this? We removed "likely".

# Line 398: "global N inventory constant": does not appear to be the case in Fig. 9a?

We discuss here changes in the parameters for the time period from the beginning of the simulation to simulation year 2200. To be more clear we slightly rephrased the sentence:

**"Until the year 2200**, changes in circulation and climate are likely the main cause for the reduction in preformed N and P in the *Ref* simulation since global N and P inventories were **almost** constant **in this time period** (Fig 9a, solid red and black line)." (Line 412)

# Line 399: Physical response: potentially summarize physical response earlier, perhaps right after 4., as this is the baseline response of the scenario which applies to all variables?

Thank your for your suggestion. Here in this manuscript we mainly focus on changes in the P cycle and therefore we would prefer to discuss changes in the meridional overturning later.

Line 400: is this the max of the global meridional overturning? Yes it is the maximum. We replaced "meridional overturning" by "meridional overturning maximum".

# Line 402: "consistent with reduction of export": in section 4.1 you appear to conclude that warmer temperatures enhance remineralization in the shallower ocean which reduces export?

We do not agree with your thoughts. An increased remineralization rate could also lead to faster recycling of nutrients from the shallow ocean to the surface ocean. This could increase the export production, because of the faster "recycling" of nutrients from the shallow ocean to the surface in comparison of the recycling of nutrients from the deep ocean to the surface for lower remineralization rates. The stratification due to the continuous warming inhibits exchange of surface waters with the deep ocean and increases the residence time of water in the ocean. Until year 2200 highest rates of warming appear in the ocean and lead to a strong stratification of the ocean, but after this CO2 emission decline and the rise in surface temperatures of the ocean is much weaker.

# Line 404-407: "speculate"? This reasoning, also in line 415, I do not understand. I would speculate that these changes are associated with older water masses. AOU and ideal age probably are highly correlated, indicating that more O2 is consumed in older waters. See literature.

We completely agree with your line of thoughts and with your conclusions, which was also reflected by the text:

"We speculate that a weaker overturning increased the residence time of water and nutrients in the surface ocean. Nutrients staying longer in the euphotic zone are with a higher probability biologically consumed. This implies more efficient utilization of nutrients and, hence, the reduction in preformed nutrients and an increase in AOU."(Line 420)

I am sorry that I do not understand your concern could you please explain yourself a bit more.

Table 1: Bur\_low and Bur\_high: reference to equation (4) rather than (3)? Bur: potentially also add coefficients here for consistency with Bur\_low, Bur\_high We improved the table as suggested.

# Figure 2a: net flux? What are the step-like increases in the Bur simulations associated with? Those are also present in subsequent figures?

We mention this already in the manuscript:

"In *Bur*, a rapid increase in the benthic P release appeared in areas where the water turned suboxic and thus drove a positive benthic feedback between P release, productivity and deoxygenation. A limited supply of P from the sediment (*Bur\_Res*) dampens this feedback."(Line 298)

Figure S2/S3: might benefit from an improved aspect ratio.

We improved the aspect ratio.

# Ocean Phosphorus Inventory: Large Uncertainties in Future Projections on Millennial Timescales and its **Consequences for Ocean Deoxygenation**

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## Abstract

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Previous studies have suggested that enhanced weathering and benthic phosphorus (P) fluxes, triggered by climate warming, can increase the oceanic P inventory on millennial time scales, promoting ocean productivity and deoxygenation. In this study, we assessed the major uncertainties in projected P inventories and their imprint on ocean deoxygenation using an Earth system model of intermediate complexity for a business-as-usual carbon dioxide (CO<sub>2</sub>) emission scenario until the year 2300 and subsequent linear decline to zero emissions until the year 3000 and hence without significant 15 differences in climate and circulation.

Model results suggest a large spread in the simulated oceanic P inventory due to uncertainties in (1) assumptions for weathering parameters, (2) the representation of bathymetry on slopes and shelves in the model bathymetry, (3) the parametrization of benthic P fluxes and (4) the representation of sediment P inventories. Our best estimate for changes in the global ocean P inventory by the year 5000

- caused by global warming amounts to +30% compared to pre-industrial levels. Weathering, benthic 20 and anthropogenic fluxes of P contributed +25%, +3% and +2% respectively. The total range of oceanic P inventory changes across all model simulations varied between +2% and +60%. Suboxic volumes were up to 5 times larger than in a model simulation with a constant oceanic P inventory. Considerably large amounts of the additional P left the ocean surface unused by phytoplankton via
- 25 physical transport processes as preformed P. In the model, nitrogen fixation was not able to adjust the oceanic nitrogen inventory to the increasing P levels or to compensate for the nitrogen loss due to increased denitrification. This is because low temperatures and iron limitation inhibited the uptake of the extra P and growth by nitrogen fixers in polar and lower latitude regions. We suggest that uncertainties in P weathering, nitrogen fixation and benthic P feedbacks need to be reduced to achieve

30 more reliable projections of oceanic deoxygenation on millennial timescales.

# 1 Introduction

Many different processes affect the oxygen balance in the ocean (e.g. oxygen solubility, stratification, respiration, circulation, Levin, 2019; Oschlies et al., 2018). Oceanic phosphorus (P) inventories are known to substantially affect oceanic oxygen inventories on millennial timescales (Tsandev and Slomp,

35 2009; Palastanga et al., 2011; Monteiro et al., 2012). Phosphorus is considered the ultimate limiting

Tronje Kemena 28.2.2019 11:40 Deleted: and Ocean Deoxygenation

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nutrient for ocean productivity at the global scale (Tyrrell, 1999). Elevated supply of P to the ocean stimulates production and export of organic matter and deoxygenation, which possibly drives more intense oxygen depletion in the oxygen deficient zones and along the continental margins, with release

- 45 of additional P from sediments turning anoxic (Van Cappellen and Ingall, 1994; Palastanga et al., 2011). Such a positive feedback was discussed for a global warming scenario under present-day conditions (Niemeyer et al., 2017) as well as for large-scale deoxygenation events in the Cretaceous era, the so-called oceanic anoxic events (OAEs) (Tsandev and Slomp, 2009; Monteiro et al., 2012; Ruvalcaba Baroni et al., 2014). For the Cretaceous, it has been suggested that atmospheric carbon
- 50 dioxide (CO<sub>2</sub>) concentrations as high as 1000 to 3000 ppmv, driven by enhanced CO<sub>2</sub> outgassing from volcanic activity (Jones and Jenkyns, 2001; Kidder and Worsley, 2012), have triggered OAEs (Damsté et al., 2008; Méhay et al., 2009; Bauer et al., 2016). The warmer climate during past OAEs increased weathering on land (Blättler et al., 2011; Pogge von Strandmann et al., 2013), leading to an enhanced supply of nutrients, in particular P, increasing the oceanic nutrient inventory and driving the positive
- 55 feedback mentioned above. Furthermore, the enhanced release of P from sediments were suggested to maintain high levels of productivity in the Cretaceous ocean (Mort et al. 2007; Kraal et al. 2010), which would contribute to the development of OAEs. Evidence in the palaeo record indicates that the Earth has experienced several OAEs with large-scale anoxia, euxinia and mass extinctions (Kidder and Worsley, 2010).
- 60 Could such OAEs also appear in the near future under contemporary global warming? High CO<sub>2</sub> concentrations in the atmosphere seem to be one driver for initiating OAEs and ocean deoxygenation. Projected anthropogenic CO<sub>2</sub> emissions may lead to atmospheric CO<sub>2</sub> concentrations exceeding 1000 ppmv at the beginning of the 22<sup>nd</sup> century if emissions continue to increase in a business-as-usual scenario (Meinshausen et al., 2011). Although anthropogenic CO<sub>2</sub> emissions occur over a short period
- compared to the long-term and relatively constant volcanic CO<sub>2</sub> emissions during OAEs (Kidder and Worsley, 2012), elevated atmospheric CO<sub>2</sub> concentrations <u>will</u> persist for many millennia (Clark et al., 2016). This may provide the conditions for long-term climate change and large-scale deoxygenation. There is thus some concern that anthropogenic CO<sub>2</sub> emissions could potentially trigger another OAE (Watson et al., 2017). Yet, Kidder and Worsley (2012) argue that emissions of global fossil fuel
- reserves are insufficient to drive a modern OAE, but may instead lead to widespread suboxia.
   During climate warming, ocean productivity could switch from P to nitrogen (N) limitation (Saltzman, 2005). N limitation could arise from enhanced denitrification in a more anoxic ocean, but at the same time low N to P ratios would be expected to stimulate N<sub>2</sub>-fixation by diazotrophs (Kuypers et al., 2004). N<sub>2</sub>-fixation in regional proximity with OMZs can lead to net N losses due to mass balance
- 75 constraints (Landolfi et al., 2013), which may even reverse the net effect of N<sub>2</sub>-fixation on the nitrogen inventory.

Recently, Niemeyer et al. (2017) showed in a model study that P weathering and sedimentary P release in a business-as-usual  $CO_2$ -emission (RCP8.5) scenario could strongly enlarge the marine P inventory and lead to a 4 to 5-fold increase in the suboxic water volume (dissolved oxygen ( $O_2$ ) concentrations

80 less than 5 mmol  $m^{-3}$ ) on millennial timescales. Here, we build on this study and test the sensitivity of the marine P and O<sub>2</sub> inventories in a climate change scenario on millennial timescales to different Tronje Kemena 28.2.2019 11:40 Deleted: had Tronje Kemena 28.2.2019 11:40 Deleted: climate OAE-like states,

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Tronje Kemena 28.2.2019 11:40 **Deleted:** During warmer and wetter climates, however, a reduced supply of acolian Fe may limit marine N<sub>2</sub>-fixation (Kidder and Worsley, 2010).

model formulations of P weathering and benthic fluxes. We aim to provide better constraints on future ocean deoxygenation and assess the biogeochemical feedbacks triggered by P addition. In Sect. 2 we

90 present the experimental design and the model parameterizations of continental P weathering and of benthic P release. In Sect. 3 we assess uncertainties in P fluxes due to different assumptions about the P weathering fluxes, different model formulations of benthic P burial and improved representation of bathymetry and anthropogenic P fluxes. Consequences for deoxygenation and for the biogeochemical cycling of nutrients are discussed.

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#### 95 2 Model and Experimental Design

## 2.1 Model

We applied the University of Victoria (UVic) Earth System Model (ESM) version 2.9 (Weaver et al., 2001), which has been used in several studies to investigate ocean oxygen dynamics (Schmittner et al., 2007; Oschlies et al., 2008; Getzlaff et al., 2016; Keller et al., 2016; Landolfi et al., 2017). The UVic model consists of a terrestrial model based on TRIFFID and MOSES (Meissner et al., 2003), an atmospheric energy-moisture-balance model (Fanning and Weaver, 1996), a sea-ice model (Bitz and Lipscomb, 1999) and the general ocean circulation model MOM2 (Pacanowski, 1996). Horizontal resolution of all model components is 1.8° latitude x 3.6° longitude. The ocean model has 19 layers

- with layer thicknesses ranging from 50 m for the surface layer to 500 m in the deep ocean. The marine 105 ecosystem was represented by a NPZD model (Keller et al., 2012). Organic matter transformations (production, grazing, degradation) were parameterized using fixed stoichiometric molar ratios (C:N:P, 106:16:1) and directly related to the production and, in oxygenated waters, utilization of O2 (O:P, 160). When  $O_2$  is depleted in the model, organic matter is respired using nitrate (NO<sub>3</sub><sup>-</sup>) (i.e. microbial denitrification). An O<sub>2</sub> concentration of 5 mmol m<sup>-3</sup> was used as the switching point from aerobic
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respiration to denitrification. Sedimentary denitrification was not considered in this model

configuration, so that water column denitrification and N2-fixation dictate the oceanic N balance. No explicit iron cycle was simulated and iron limitation was approximated with prescribed seasonally varying dissolved iron concentrations (Keller et al., 2012). Parameterizations of benthic and weathering fluxes of P were extended from the study of Niemeyer et al. (2017). Implementations of a calcium

115 carbonate sediment model (Archer, 1996) and a parameterization for silicate and carbonate weathering (Meissner et al., 2012) were applied in all simulations. When P weathering and anthropogenic P fluxes were applied (see Sect. 2.2), the global P flux was distributed over all river basins, in every grid box, weighted by river discharge rates.

# 2.2 Experimental Design

120 Twelve different model simulations were performed to explore the range of uncertainties for the longterm development of the oceanic P inventory (Table 1). Each simulation started from an Earth system state close to equilibrium under preindustrial atmospheric CO<sub>2</sub> concentrations, prescribed wind fields and present-day orbital forcing. Spin-up runs lasting 20,000 simulation years or longer were made for each simulation to reach equilibrium. In the spin-up runs for simulations with benthic P burial (purple

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and red in Table 1), the marine P inventory was kept constant by instantaneously compensating oceanic P loss (burial) by P weathering fluxes to the ocean. For model simulations without benthic P <u>burial</u>

- 130 (black and blue in Table 1), one common spin-up run was performed without P weathering fluxes.
  All transient simulations started in the year 1765 and ended in <u>the</u> year 5000. Simulations were forced with anthropogenic CO<sub>2</sub> emissions (fossil fuel and land use change) according to the extended RCP 8.5 scenario until the year 2300 (Meinshausen et al., 2011), followed by a linear decline to zero CO<sub>2</sub> emissions by the year 3000. Warming from non-CO<sub>2</sub> greenhouse gases and the effect of sulphate
- 135 aerosols were prescribed as radiative forcing (Eby et al., 2013). Non CO<sub>2</sub>-emission effects from landuse change were not considered. The reference simulation (*Ref*) was performed without weathering and without burial fluxes of P, meaning that the P inventory of the ocean remained unchanged. The remaining transient simulations applied either variable climate-sensitive weathering anomalies (without burial) or time-variable burial fluxes (with constant weathering) to the ocean (Table 1).

## 140 2.3 Burial experiments

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The water column model is not coupled to a prognostic and vertically resolved sediment model. Instead, <u>sinking organic matter interacts with the sediment via "transfer functions" (Wallmann, 2010)</u> on a detailed subgrid bathymetry (Somes et al., 2013). Sinking organic matter is partially intercepted at the bottom of each grid box by a sediment layer and the intercepted amount depends linearly on the

145 <u>fractional coverage of the grid box by seafloor. The intercepted organic P is remineralized in accordance with Eq. (1) and Eq. (2), whereby organic C and N are completely remineralized under oxygen or nitrate utilization without any burial.</u>

Fractional coverage of every ocean grid box by seafloor was calculated on each model depth level according to the subgrid bathymetry (Somes et al., 2013). The subgrid bathymetry was inferred from

ETOPO2v2<sup>1</sup> (National Geophysical Data Center, 2006). ETOPO2v2 has a horizontal resolution of 2-minutes fine enough to adequately represent continental shelves and slopes. The coarse standard model bathymetry in the UVic model has a horizontal resolution of 1.8° latitude x 3.6° longitude.
 P burial in the sediment (*BUR<sub>p</sub>*) was determined in every grid box with sediment from the difference

between the simulated detritus P rain rate to the sediment  $(RR_P)$  and the benthic release of dissolved inorganic P from the sediment  $(BEN_P)$ :

 $RIIR_{-} = RR_{-} - RI$ 

$$UR_P = RR_P - BEN_P \tag{1}$$

where  $RR_P$  is the detritus flux from the ocean (in P units).  $BEN_P$  was calculated locally by a "transfer function", which parameterizes sediment/water exchange of P as a function of the rain rate of organic matter and the bottom water O<sub>2</sub> concentration. Preferential P release, relative to carbon (C), is observed in sediments overlain by O<sub>2</sub>-depleted bottom waters (Ingall and Jahnke, 1994). Benthic P release was dependent on the dissolved inorganic carbon release ( $BEN_C$ ) from organic matter degradation in the sediment and the C:P regeneration ratio  $r_{C:P}$  (Wallmann, 2010; equation 2):

atio 
$$r_{C:P}$$
 (Wallmann, 2010; equation 2):  
 $BEN_P = \frac{BEN_C}{r_{C:P}}.$ 

<sup>1</sup> https://www.ngdc.noaa.gov/mgg/global/etopo2.html

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(2)

 $BEN_C$  was computed (Eq. 3a) as the difference of the carbon rain rate to the sediment ( $RR_C$ ) and a 'virtual' organic carbon burial flux ( $BUR_C$ ). Virtual is meant in the sense that there is no explicit burial

of organic C in the model, and instead all organic C is remineralized in the deepest ocean layer. In this study we do not focus on changes in the C inventory and therefor  $BUR_C$  is just calculated to determine <u>BEN\_C</u> in Eq. (2).  $BUR_C$  is dependent on the simulated organic C rain rate and bathymetry (Flögel et al., 2011). Burial of organic C is more efficient on the shelf and continental margins (Eq. 3b) than for the deep sea (Eq. 3c, sediment below 1000m water depth):

$$BEN_C = RR_C - BUR_C. \tag{3a}$$

$$BUR_{C} = 0.14 \cdot RR_{C}^{1.11}, \tag{3b}$$

$$BUR_c = 0.014 \cdot RR_c^{1.05},$$

170 where  $RR_C$  is in mmol C m<sup>-2</sup> a<sup>-1</sup>.  $r_{C:P}$  (in Eq. 4) depends on the bottom water oxygen concentration and was calculated according to (Wallmann, 2010; equation 4).

$$r_{C:P} = Y_F - A \cdot \exp(-O_2/r).$$
 (4)

where  $O_2$  is in mmol m<sup>-3</sup> and the coefficients and their uncertainties are  $Y_F$ =123±24; A=112±24; r=32±19 mmol m<sup>-3</sup>. Under high  $O_2$  conditions  $r_{C:P}$  is 123, which is close to the Redfield ratio of 106. Under low  $O_2$  conditions,  $r_{C:P}$  is lower than 106, which leads to a preferential P release from organic matter and, eventually, a net release of P from the sediment ( $BEN_P > RR_P$ , in Eq. 1).

Burial fluxes of P were applied in the simulations *Bur*, *Bur Dun*, *Bur low*, *Bur high*, *Bur noSG* and *Bur res*. The default *Bur* model configuration uses Eq. (3) (Flögel et al., 2011) and the subgrid-scale bathymetry. Uncertainties in benthic P <u>burial</u> were examined by modifying this default model configuration.

180 In the *Bur\_Dun* (i.e. burial parameterization from Dunne et al. 2007) simulation  $BUR_C$  was calculated using Eq. (5) with  $RR_C$  in mmol C m<sup>-2</sup> d<sup>-1</sup>; Dunne et al. (2007):

$$BUR_{c} = RR_{c} \cdot \left[ 0.013 + \frac{0.53 \cdot RR_{c}^{2}}{(c + RR_{c})^{2}} \right].$$
(5)

Where  $c = 7 \text{ mmol C m}^2 \text{ d}^{-1}$ . This parameterization leads to high (low) organic C burial rates for high (low) organic C rain rates. This formulation is different to the standard formulation of burial in Eq. (3b, c) where burial depends on the C rain rates and in addition on the water depth. In the standard

185 formulation, C burial is <u>by definition one</u> magnitude larger in slope and shelf regions compared to the deep ocean<u>\_(see Eq. 3b, c).</u>

We examined the sensitivity of P burial to the uncertainty of the parameters in Eq. (4) describing the carbon to phosphorus regeneration ratio  $r_{C:P}$ . Given means and standard deviations for the parameters  $Y_F$ =123±24; A=112±24; r=32±19 and assuming a Gaussian distribution, 100,000 independent coefficient combinations were assembled to calculate offline a range of global P burial estimates. For

- the offline calculation, preindustrial fields of  $O_2$  and  $RR_C$  were extracted from the simulation *Bur* with a temporal resolution fine enough to resolve seasonal variations in the data. Global P burial varied between 0.21 TmolP a<sup>-1</sup> (*Bur\_low*) and 0.60 TmolP a<sup>-1</sup> (*Bur\_high*) for a confidence interval of 90% (coefficients are shown in Table 1). Individual spin-ups were performed for the *Bur\_low* and *Bur\_high*
- simulation to check that the offline calculated P burial corresponded to the online values from the spinup. Only minor differences between the O<sub>2</sub> fields of the *Bur* spin-up and the spin-ups for *Bur low* and

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calculated using the coarser standard model bathymetry, which barely reproduce the global coverage of shelf areas (compare hypsometries in suppl. Fig. S1). Tronje Kemena 28.2.2019 11:40

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(3c)

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*Bur\_high* simulations were noted (not shown), which implies negligible errors in the offline calculation of the preindustrial global P burial.

For the simulation Bur noSG (i.e. without subgrid-scale parameterization), P fluxes at the sediment-

The implemented transfer functions (Eq. 2 and 4) assume unlimited local reservoirs of sedimentary P,

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# ocean interface were calculated using the coarser standard model bathymetry, which barely reproduce the global coverage of shelf areas (compare hypsometries in suppl. Fig. S1). This does not affect other processes like circulation, advection or mixing.

meaning that the cumulative release of P may exceed the local inventory of P in the sediment if the benthic <u>release is</u> sustained over a longer period of time. In the simulation *Bur\_res* (i.e. restricted release or P reservoir) we tested the impact of this simplification by applying sediment inventory

- 250 release or P reservoir) we tested the impact of this simplification by applying sediment inventory restrictions to sediment P release. In accordance to Flögel et al. (2011), release of P from the deeper ocean (>1000 m) cannot exceed the rain rate of organic P to the sediment. For the continental shelf and slope, an upper limit sediment P inventory was calculated based on the following assumptions. We assume that the top 10 cm of the sediment column are mixed by organisms and are hence regarded as
- 255 the active surface layer that is in contact with the overlying bottom water. Considering a mean porosity of 0.8 and a mean density of dry particles of 2.5 g cm<sup>-3</sup>, the mass of solids in this layer is 5 g cm<sup>-2</sup> (Burwicz et al., 2011). The mean concentration of total P in continental shelf and slope sediments is 0.07 wt-% equal to 22.6  $\mu$ mol/g (Baturin, 2007). Together, these assumptions convert to a maximum local inventory of total solid P in the active surface layer of <u>*RESp*,max</u> = 113  $\mu$ mol cm<sup>-2</sup> (Eq. 6a). We

assume that shelf and slope sediments can release up to 100 % of the total solid P under low oxygen conditions. The Jocal P inventory ( $RES_P$ ) can be fully replenished by P supply from the water column, and any excess P is assumed to be permanently buried:

$$[RES_{P} \in \mathbb{R} \mid 0 \ge RES_{P} \ge RES_{P,max}]$$

$$\frac{\Delta RES_{P}}{\sqrt{\Delta t}} = RR_{P} - BEN_{P}$$
(6b)

Local values of *RES<sub>P</sub>* adjust during the spin-up according to the environmental conditions. Our pragmatic sediment inventory approach most likely overestimates the upper limit of P that can be
 released from the sediments. For example, under low O<sub>2</sub> conditions, part of the releasable or reactive P is transformed into authigenic P and permanently buried (Filippelli, 2001).

All *Bur* experiments applied a constant global weathering flux ( $W_{P,const}$ ) as established during the respective spin-up run (see Table 1 for values of  $W_{P,const}$  for the different *Bur* experiments).

$$W_P = W_{P,const} \tag{7}$$

## 2.4 Weathering Experiments

Uncertainties in the ocean P inventory due to weathering processes and anthropogenic fluxes of P were examined with the model simulations *Anthr, Weath0.05, Weath0.10, Weath0.15* and *Weath0.38*.
In simulations *Weath0.05, Weath0.10, Weath0.15, Weath0.38* (i.e. the number represents the preindustrial weathering flux) the global weathering flux of P to the ocean (*W<sub>P</sub>*) was parameterized in terms of an anomaly relative to a preindustrial P weathering flux (*W<sub>P,Q</sub>*) according to Eq. (8).

$$W_P = W_{P,0} \cdot (f(NPP, SAT) - 1). \tag{8}$$

# Tronje Kemena 28.2.2019 11:40 Deleted: . Tronje Kemena 28.2.2019 11:40 Deleted: this Tronje Kemena 28.2.2019 11:40 Deleted: inventory ( $RES_P$ ) Tronje Kemena 28.2.2019 11:40 Deleted: reservoir Tronje Kemena 28.2.2019 11:40 Deleted: $\_Any$ Tronje Kemena 28.2.2019 11:40 Deleted: $\_ARS_P$ Tronje Kemena 28.2.2019 11:40 Deleted: $BEN_P; 0 \ge RES_P \ge 113 \ \mu mol/_{cm^2}$ Tronje Kemena 28.2.2019 11:40 Deleted: $BEN_P; 0 \ge RES_P \ge 113 \ \mu mol/_{cm^2}$ Tronje Kemena 28.2.2019 11:40

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The weathering function f is given in Eq. (9). Values of  $W_{P,0}$  are given in Table 1 and derived below. The chosen anomaly approach assumes that, at steady state,  $W_{P,0}$  is balanced by a respective global burial flux and hence can be neglected during the spin-up. In these simulations no benthic P <u>burial was</u>

applied and for preindustrial conditions the weathering function f(NPP,SAT) equals 1 and hence  $W_P$ 

equals 0 TmolP  $a^{-1}$ . The dynamic weathering function f (Eq. 9) was adopted from Niemeyer et al.

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(2017) and is originally based on an equation from Lenton and Britton (2006) for carbonate and silicate weathering. Following Niemeyer et al. (2017), we assumed that the release of P is proportional to the chemical weathering of silicates and carbonates on a global scale. Equation (9) describes the sensitivity of terrestrial weathering to the change of global terrestrial net primary production (*NPP*) and global

mean surface air temperature (SAT):

$$f = 0.25 + 0.75 \cdot (NPP/NPP_0) \cdot (1 + 0.087(SAT - SAT_0)).$$
(9)

with  $NPP_0$  and  $SAT_0$  being the respective preindustrial values. Increasing SAT and NPP lead to enhanced weathering. The upper estimate of  $W_{P,0}$  in *Weath0.38* was inferred from the P burial reference simulation *Bur*, assuming that the global integral of burial is compensated by the preindustrial global weathering flux (i.e. the global marine P inventory is in steady state). With the simulations *Weath0.05*, *Weath0.10*, *Weath0.15*, *Weath0.38* we explored the range of  $W_{P,0}$  estimates as derived from

- observational studies, which range from 0.05 to 0.30 TmolP a<sup>-1</sup> (see Fig. 1, Benitez-Nelson, 2000; Compton et al., 2000; Ruttenberg, 2003). These studies <u>give a range of</u> total P fluxes to the oceans<u>which</u> are higher than interfered from dissolved inorganic P fluxes<u>shown already in previous studies</u>
- 305 (e.g. Martin and Meybeck, 1979; Rao and Berner, 1993) and in the Global News Model (Seitzinger et al., 2005). A small amount of fluvial P is delivered to the ocean as dissolved inorganic P, but the majority (90%) is particulate (inorganic and organic) P (Compton et al., 2000). The fast transformations between dissolved and particulate P in rivers (seconds to hours) (Withers and Jarvie, 2008) suggest a much higher amount of P that is available for marine organism than derived from
- 310 dissolved inorganic P concentrations. A large amount of bioavailable P in rivers is present as loosely sorbed and iron-bound P. Estimates of bioavailable P are given in Fig. 1 (Benitez-Nelson, 2000; Compton et al., 2000; Ruttenberg, 2003), which are much higher than the estimates for dissolved inorganic P (0.018 TmolP a<sup>-1</sup> from Seitzinger et al. (2005) or 0.03 TmolP a<sup>-1</sup> from Filippelli (2002)). Taking into account only fluxes of dissolved inorganic P would strongly underestimate the effect of
- 315 weathering fluxes as a P source to the ocean. The weathering parametrization (Eq. 9) was used to scale preindustrial fluxial fluxes of bioavailable P that is delivered in UVic to the ocean as dissolved inorganic P. In the model, no distinction was made between particular and dissolved fluxial fluxes of P. Uncertainties to other weathering parameterizations were not investigated in this study. Our parameterization predicts similar weathering rates to other weathering formulations (Meissner et al.,
- 2012, their Fig. 6a). Since weathering is calculated on a global scale, we cannot study the effects of regional lithology and soil shielding on weathered P (Hartmann et al., 2014). UVic neither resolves the P cycle in the rivers, which is an active field for scientific research (Beusen et al., 2016; Harrison et al., 2019).

Finally, global anthropogenic P fluxes from fertilization, soil loss due to deforestation and sewage as projected by Filippelli (2008) were prescribed in the simulation *Anthr<sub>e</sub>*(anthropogenic). Tronje Kemena 28.2.2019 11:40

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## 330 3. Uncertainties in Phosphorus Inventory

The large range of projected global phosphorus (P) fluxes to the ocean from sediments or weathering (Fig. 2a) leads to uncertainties in future P inventories by up to 60% of the present-day value until the year 5000 (Fig. 2b). All simulations show negligible differences in atmospheric  $CO_2$  concentrations and hence undergo a similar climate development. Maximum  $CO_2$  concentrations of 2200 ppmv were

335 reached in the year 2250 and then declined to 1100 ppmv by the year 5000, comparable to results from Clark et al. (2016),

## 3.1. Fluvial P Fluxes: Weathering and Anthropogenic

Largest uncertainties in the P inventory are related to the large range of P weathering fluxes (Fig. 2, blue curves). Upper and lower estimates of P weathering fluxes differ by a factor of 6 (Fig. 2a, blue

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lines). In our weathering simulations, weathering anomalies depend linearly on the preindustrial weathering flux,  $W_{P,0}$ , estimate (see Eq. 8) because the climate development is <u>essentially</u> equal across the simulations. Therefore, the choice of  $W_{P,0}$  (Fig. 1a) is a major source of uncertainty for projected future land-ocean P fluxes.

Weathering fluxes increased from the pre-industrial value by a factor of 2.5 until <u>the</u> year 5000 for atmospheric CO<sub>2</sub> concentrations of 1100 ppmv. This is comparable with the two- to four–fold increase

- in weathering fluxes estimated during OAE 2 approximately 91 Ma ago (Pogge von Strandmann et al., 2013) when atmospheric CO<sub>2</sub> concentrations increased to about 1000 ppmv (Damsté et al., 2008).
   In contrast to weathering-induced P input, anthropogenic P fluxes (Filippelli, 2008) influence the
- global marine P inventory only in the near future (Fig. 2a, black dashed line). A decline in
  anthropogenic P fluxes after the year 2100 is expected due to the depletion of the easily reachable phosphorite mining reserves (Filippelli, 2008).

## 3.2. Sediment Fluxes: Parameterizations, Subgrid Bathymetry, Sediment Reservoir

- The release of P from the sediment is strongly dependent on the O<sub>2</sub> concentration in the water above the sediments (Wallmann 2003; Flögel et al. 2011). Climate warming reduces O<sub>2</sub> solubility and ventilation of the ocean, which decreases the global O<sub>2</sub> content (more details in Sect. 4). The general decrease in ocean O<sub>2</sub> content may therefore cause preferential release of P from marine sediments. Differences in sediment P fluxes in our simulations are related to uncertainties in the parameterization of the transfer function (Fig. 2, red lines, -0.01 to 0.22 TmolP a<sup>-1</sup> by the year 5000), to different representations of the bathymetry (Fig. 2, purple dashed line, 0.06 (without subgrid) and 0.12 (*Bur*)
- 360 TmolP a<sup>-1</sup>) and to the way sediment P reservoirs in the sediment are represented (Fig. 2, purple solid line, -0.01 (limited reservoir) and 0.12 (unlimited reservoir, *Bur*) TmolP a<sup>-1</sup>). The global P burial of approximately 0.2 TmolP a<sup>-1</sup> (Fig. 3) (Filippelli and Delaney, 1996; Benitez-Nelson, 2000; Ruttenberg, 2003) is relatively well reproduced by simulations *Bur\_low* and *Bur\_Dun*. The simulation with the standard UVic bathymetry (*Bur\_noSG*) underestimates P burial by 60% while
- 365 the simulations Bur\_high, Bur and Bur\_res overestimate P burial by 180%, 90% and 80% with respect to estimates based on observations. The transient response of the P release to O<sub>2</sub> was stronger for simulations with low burial and vice versa (Fig. 2), except for simulation Bur\_res. In Bur\_res, a

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- significant reduction in the transient P release occurred due to the implementation of a finite P
   375 reservoir, with net global P loss due to enhanced burial at the end of the simulation. In the year 5000, global P concentrations increased in *Bur\_res* by only 0.06 mmolP m<sup>-3</sup> compared to the global mean pre-industrial concentration of 2.17 mmolP m<sup>-3</sup>. This is six-fold smaller than the increase of 0.36 mmolP m<sup>-3</sup> in simulation *Bur* with an assumed unlimited P reservoir. The small increase in the oceanic P inventory in *Bur\_res* can be explained by the reduction in P sediment inventory rather than by changes
- 380 in the rain rate of particulate organic matter to the sediment  $(RR_C)$ . In *Bur*, a rapid increase in the benthic P <u>release</u> appeared in areas where the water turned suboxic and thus drove a positive benthic feedback between P release, productivity and deoxygenation. A limited supply of P from the sediment (*Bur\_Res*) dampens this feedback.
- Simulated pre-industrial  $RR_C$  increased significantly from 180 to 1040 TgC a<sup>-1</sup> on the shelf and globally from 900 to 1500 TgC a<sup>-1</sup> compared to simulations without subgrid bathymetry. Pre-industrial  $RR_C$ with subgrid bathymetry agrees better to estimates by Bohlen et al. (2012) (Table 2) and to other field data studies reporting a range from 900 to 2300 TgC a<sup>-1</sup> (Fig. 4) (Muller-Karger et al., 2005; Burdige, 2007; Dunne et al., 2007; Bohlen et al., 2012)
- In summary, subgrid bathymetry leads to a substantial improvement of the representation of *RR<sub>C</sub>* to the
  sediment. More realistic benthic fluxes of P could be also attained by adjusting parameters for *r<sub>C:P</sub>* (Eq. 4) or by using the function of Dunne et al. (2007) to calculate *BUR<sub>C</sub>* (Eq. 5). The implementation of a finite P reservoir in the sediment has a substantial impact on the transient development of the global P inventory on millennial time scales.

## 4. Ocean Deoxygenation and Suboxia

- Climate change influences ocean oxygen content by changes in circulation, ocean temperature and the degradation of organic matter. In warming surface waters, the solubility of O<sub>2</sub> decreases along with an increase in stratification, which together cause the deeper ocean to becomes less ventilated (Bopp et al., 2002; <u>Matear and Hirst, 2003</u>; Oschlies et al., 2018; <u>Shaffer et al., 2009</u>). Changes in export production and the degradation of organic matter in the ocean interior also affects O<sub>2</sub> content. In the following, we analyze the impact of different ocean P inventories on ocean deoxygenation and suboxia (Fig. 5). For a
- more detailed analysis we compare *Weath0.15* to the *Ref* simulation. In the *Weath0.15* simulation, the assumed preindustrial weathering flux compares well to estimates from observations (Fig. 1). In the *Ref* simulation, global suboxic volume increased due to climate change from 0.3 to 1% until the
- year 5000 and the suboxic sediment area increased from 0.06 to 0.23% (Fig. 5, black line). In the
   *Weath0.15* simulation, the increase in suboxic volume (suboxic sediment area) was more than 2 (3) times higher than for the *Ref* simulation. The expansion of suboxic sediment areas was also enhanced for simulations with benthic fluxes, which could be related to regional feedbacks between increasing marine productivity, decreasing oxygen and enhanced sedimentary P release (Tsandev and Slomp, 2009). The explicitly simulated finite sedimentary P reservoir in simulation *Bur res* places an upper
- 410 limit to the benthic release of P and dampens these regional feedbacks, resulting in a weaker spreading of suboxic waters by only 17% compared to the *Ref* simulation.

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In the following sections, we show how the expansion of suboxia is related to net primary production in the ocean (NPP), the export of organic matter (Sect. 4.1) and to nitrogen limitation (Sect. 4.2). Finally, we show how changes in O2 solubility and utilization vary over time and affect the global O2

420

inventory (Sect. 4.3). The latter approach gives another perspective because changes in  $O_2$  inventories are a global integrated signal in comparison to the extent of suboxia, which are a consequence of more local processes.

# 4.1. Enhanced Biological Pump

The biological carbon pump can be summarized as the supply of biologically sequestered CO<sub>2</sub> to the 425 deep ocean. In the euphotic zone phytoplankton and diazotrophs take up CO<sub>2</sub>, a process that is intensified by elevated PO<sub>4</sub> concentrations in the surface ocean (Fig. 6a). Part of the organic matter sinks out of the euphotic zone (Fig. 6b) to the ocean interior, where it is respired using O<sub>2</sub>. It is therefore P supply to the surface waters that explains the differences in deoxygenation between the simulations. Circulation changes could also affect the supply of O2 to the ocean interior. However, no 430 significant differences in climate and circulation appeared among the simulations and therefore the

global-warming induced circulation changes affected all simulations in the same way. In the Ref simulation, net primary production (NPP, Fig. 6a black line) increased from 45 to 70 TmolP a<sup>-1</sup> (57 to 89 GtC a<sup>-1</sup>) by the end of the simulation. In Weath0.15, enhanced P supply to the ocean led to a doubling of NPP compared to the Ref simulation. The P inventory increased continuously, but NPP

- 435 did not follow this trend and instead peaked in the year 4000. In the year 5000, all simulations, excluding Weath0.38, showed a similar response of NPP to the P addition with an increase in NPP of 19 TmolP a<sup>-1</sup> (relative to the Ref simulation) per 10% increase in P inventory. In Weath0.38 the response was weaker and NPP increased by 8 TmolP a<sup>-1</sup> per 10% rise in the P concentration. P is less effectively utilized in simulations with large oceanic P inventories. Higher ocean temperatures
- 440 enhanced remineralization of organic matter in the shallower ocean so that the overall export to NPP ratio decreased from its preindustrial value of 0.12 to an average value among all simulations of 0.08 by the year 5000. To summarize, NPP and export of organic matter is sensitive to P addition. However, the proposed positive feedback between P, NPP, export of organic matter, and deoxygenation was limited in our simulations due to a negative feedback related to nitrate availability. This is shown and explored in the following section.

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# 4.2. Nitrogen Limitation

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At the end of the spin-up the N sink by denitrification and the N source by N2-fixation were balanced. In the Ref simulation, climate warming enlarged the oxygen minimum zones, which enhanced denitrification in the tropics (not shown). In our model, diazotrophs are limited by P and Fe and are not limited by N. Their growth rate, which depends on temperature being zero below 15°C, is slower relative to non-fixing phytoplankton. These characteristics allow them to succeed in warm, low-N and high-P environments that receive sufficient iron. In all simulations, N2-fixation was stimulated by the addition of P to the ocean and was sensitive to rapid changes in the supply of P (compare Fig. 7a and Fig. 2a). However, N2-fixers (Fig. 7a) were not able to use the extra P supply in polar and iron limited

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- 460 regions where low temperatures and iron limitation, respectively inhibit their growth (Fig. 8). This lead to a substantial amount of excess phosphate in the surface waters of these regions (Fig. \$2). Because N2 fixers were not able to balance the loss by denitrification, nitrate decreased globally by 4 mmolN m <sup>3</sup> until the year 5000 (Fig. <u>7b)</u>. The loss in nitrate led to a decrease in globally averaged N to P ratios. In the Ref simulation, N:P decreased from 14 to 12 and for the Weath0.15 simulation it decreased to 10,
- 465 which contributed further to a N limiting ocean. The nitrogen cycle was not able to recover from the decrease in N:P ratio with respect to pre-industrial values. We acknowledge that in the current study we did not account for potential future changes in iron concentrations (from atmospheric deposition, shelf inputs) and that the lack of a fully prognostic iron model may lead to a different sensitivity of the response of diazotrophs. Similarly we did not account for the ability of phytoplankton to adapt to changing N:P ratios, that may affect marine biological productivity and in turn deoxygenation. These
- 470

would require further studies.

# 4.3. Temporal Variations of Deoxygenation

Anomalies in circulation, ocean temperature and remineralisation of organic matter affect oceanic O2 levels in a climate-warming scenario. In the Ref simulation, the O<sub>2</sub> inventory (Fig. 9a) decreased by 60 475 Pmol  $O_2$  by the year 3000 and then reached present day values again by the year 5000. In Weath 0.15, weathered P enhanced deoxygenation and led to a greater decrease in O2 than in the Ref simulation. The  $O_2$  decrease was up to 70 Pmol in the year 3300 and  $O_2$  still showed a negative anomaly of 24 Pmol O<sub>2</sub> by the year 5000. Global anomalies in oxygen were due to changes of the Apparent Oxygen Utilization (AOU, Fig.  $\frac{9}{2}$ ) and the O<sub>2</sub> saturation level (Fig.  $\frac{9}{2}$ ). AOU is calculated from the difference 480 between the O2 saturation concentration and the in situ oxygen concentration assuming that all ocean water leave the surface layer saturated in O2. The calculation of AOU is in general biased to higher values, because in polar regions surface water leaves the surface water in respect to oxygen in a undersaturated state due to reduced air-sea gas transfer inhibited by sea ice (Ito et al., 2004). In UVic

- this leads to an overestimation of AOU by 30% (Duteil et al., 2013). For a warming ocean sea ice cover 485 reduces which converts into an underestimation of the AOU anomaly in Fig. 9c. Changes in O2 saturation were similar across the model simulations and followed with a delay surface ocean temperature. The circulation and ventilation of the ocean were similar in the model simulations because differences in surface temperatures were negligible and the atmospheric forcing of the ocean circulation was identical so that differences in AOU depended almost only on biological O2
- 490 consumption and AOU anomalies were directly yet inversely related to the changes in O2 levels. Hence, biological consumption explained variations in O2 content among the different model simulations (compare Fig.  $\underline{9a}$  and  $\underline{9b}$ ). Increasing O<sub>2</sub> utilization contributed to the decrease of the O<sub>2</sub> until the year 3000. Thereafter, a distinct negative trend in AOU with a similar slope was observed among all simulations and contributed to a re-oxygenation of the ocean. For simulations with larger P 495 inventories, the AOU had a larger positive offset to the Ref simulation.

In a model with constant stoichiometry for elemental exchange by biological processes, anomalies in AOU (Fig. 10, blue lines) can be explained by the difference between total integrated nutrients (Fig. <u>10</u>, red and black solid lines as anomalies) and preformed nutrients (Fig. <u>10</u>, red and black dashed lines

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as anomalies). Preformed nutrients correspond to the fraction that leaves the surface ocean unutilized by phytoplankton. For example in the Southern Ocean, a large fraction of nutrients leaves the surface

530 as preformed nutrients. The fraction of utilized and preformed nutrients can change during a transient simulation and could affect the oxygen state of the ocean.

In the *Ref* simulation (Fig.  $\frac{10a}{10a}$ ), the anomaly of preformed dissolved inorganic P was directly inverse to the anomaly of AOU because the oceanic P Inventory was conserved in this simulation. Until the year 2200, changes in circulation and climate are the main cause for the reduction in preformed N and

- P in the *Ref* simulation since global N and P inventories were <u>almost</u> constant in this time period (Fig 9a, solid red and black line). During continuous and intense ocean warming, a weakening of the meridional overturning (not shown) reduced ocean ventilation. The meridional overturning <u>maximum</u> decreased from 17 Sv (pre-industrial) to 11 Sv in <u>the</u> year 2200. The continuous warming and stratification of the ocean reduces the supply of nutrients to the surface layer from the deep ocean. This
- 540 is consistent with a reduction of the export of organic matter until the year 2200 (Fig. 6b). The balance between exported P out of the surface ocean and supplied P controls changes in AOU. We speculate that a weaker overturning increased the residence time of water and nutrients in the surface ocean. Nutrients staying longer in the euphotic zone are with a higher probability biologically consumed. This implies more efficient utilization of nutrients and, hence, the reduction in preformed nutrients and an 545
- 545 increase in AOU.

Enhanced suboxia after <u>the</u> year 2200 drove excess denitrification and a decline in nitrate (Fig. <u>10a</u> red solid line) in the *Ref* simulation. The decline in nitrate could explain the negative trend in AOU anomalies (Fig. <u>10a</u> blue solid line) and therefore a negative feedback on the global deoxygenation. In the year 2200, overturning had started to recover quickly and increased to 21 Sv in the year 3000

- 550 (+24% relative to preindustrial values), which drove a faster overturning of organic matter in the surface ocean and a decrease in global AOU. We assume that the slight increase in export by 5% (relative to preindustrial values) was not strong enough to compensate for the by +24% faster overturning, which reduced the residence time of nutrients in the surface ocean.
- P addition in the *Weath0.15* simulation stimulated N<sub>2</sub>-fixation by diazotrophs and counteracted N-loss
  by denitrification (Fig. <u>10b</u>, red solid line). This led to an increase in N inventory by 17 Pmol O<sub>2</sub>-equivalents compared to the *Ref* simulation. Furthermore, the high availability of P seems to reduce preformed N by 6 Pmol O<sub>2</sub> equivalents. Both explain the difference in AOU between *Weath0.15* and *Ref* of 24 Pmol O<sub>2</sub> at the end of the simulation (Fig. <u>9b</u>). However, denitrification still exceeded N<sub>2</sub>-fixation, which led to low levels of nitrate. From the year 5000 approximately all of the added P in the
- 560 Weath0.15 simulation remained unused by phytoplankton, left at the surface ocean as preformed P and was afterwards stored in the deep ocean. Phytoplankton was not able to utilize the <u>extra P</u> because it was limited in nitrate. Diazotrophs were not able to compensate for the lack in N due to iron limitation and low surface temperatures in the polar oceans. The denitrification feedback driven by the spread of suboxic conditions in the tropics had reduced further N availability for the phytoplankton and reduced the effect of P addition on the global oxygen level.

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# 5. Discussion and Conclusions

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The P inventory is very sensitive to the weathering and benthic flux parameterizations tested in our model. Large uncertainties (Fig. 2, blue lines) derive from poorly constrained estimate for the preindustrial P weathering flux that ranges from 0.05 to 0.30 Tmol P  $a^{-1}$  (Benitez-Nelson, 2000; Compton et al., 2000; Ruttenberg, 2003). The preindustrial weathering flux in simulation *Weath*0.15 (0.15 Tmol P  $a^{-1}$ ) is well in this range. In this simulation, enhanced weathering leads to an increase in the global ocean P inventory by 25% until the year 5000 (Fig. 2, blue dotted line). Benthic fluxes of P

were simulated using transfer functions on a subgrid bathymetry. Applying the transfer functions without taking into account the local sedimentary P inventory can greatly overestimate the release of benthic P on long time scales. In the UVic model, the application of finite benthic P inventories limited the benthic release significantly. Under low-oxygen conditions, sediments were P depleted already after a few years to decades. In our simulation, this resulted in an increase in the global oceanic P

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inventory by just 3% (Fig. 2, magenta solid line). This <u>could imply</u> that benthic release of P is actually negligible in comparison to the weathering fluxes of P, but the UVic model does not resolve coastal processes such as the deposition of reactive particulate P from rivers on the continental shelves and its dissolution and release to the water column. For a more realistic comparison of benthic and fluvial P fluxes, a more detailed representation of coastal processes would be necessary to simulate deposition

- and release of fluvial P<sub>v</sub>from the sediments at the shelf. However, we can conclude that the actual local inventories of P are too small to sustain a positive benthic P feedback over several millennial. Further, we find that a more realistic bathymetry substantially improves the simulated rain rate of particular organic carbon to the sediment (Table 2), particularly on the shelf, which most models do not resolve. Anthropogenic P fluxes increased the global P inventory by just 2% (Fig. 2, black dashed line). In
- summary, our best estimate for changes in the total global ocean P inventory by the year 5000 amounts to +30%, which was dominated by weathering. This seems to be surprisingly high, but several studies indicate that changes in past climate could also have been accompanied with substantial changes in the P inventory but at a much lower pace (Planavsky et al., 2010; Monteiro et al., 2012; Wallmann, 2014). In this simple addition of the P inventories we cannot account for feedbacks, which would appear in a fully coupled model. For such high P inventories we would expect larger suboxia and therefore more P release from sediments and at the same time a stronger export of organic P that lead to increased P burial.
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The increased P inventory (Fig. 2b) promotes deoxygenation (Fig. 5) and expansion of suboxia, but it also causes a net loss of nitrate, which appears to further limit the full utilization of P by phytoplankton in our simulations. Wallmann (2003), using a box model, already recognized that for a eutrophic ocean, nitrate might ultimately limit marine productivity. As a consequence, large amounts of P leave the surface ocean as preformed P (Fig. 10b) with no further impact on O<sub>2</sub> levels in the ocean interior. Low N/P ratios are thought to give N<sub>2</sub>-fixers a competitive advantage over ordinary phytoplankton and lead to an increase in N<sub>2</sub>-fixation (Fig. 7a). In the time period of the OAE1a and the OAE2, a substantial increase in N<sub>2</sub>-fixation was also inferred from measurements of sediment nitrogen isotope

compositions typical for newly fixed nitrogen conditions and from high abundances of cyanobacteria indicated by <u>a high 2-methylhopanoid index (Kuypers et al</u>, 2004). However, high denitrification rates Tronje Kemena 28.2.2019 11:40 Deleted: implies

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remove nitrate from the global ocean and in the UVic model N<sub>2</sub>-fixers are not able to compensate for this loss (Fig. 7b) because low temperatures in polar regions and iron limitation at lower latitudes

- 625 inhibit growth of diazotrophs (Fig. §) and a substantial amount of excess phosphate remains in the surface waters in these regions (Fig. §2). General circulation models without a N cycle, or box models without realistic representation of habitats suitable for N<sub>2</sub>-fixers, would miss this important negative feedback limiting global deoxygenation. As a next step it would be reasonable to investigate how different parameterizations of the N cycle and a full dynamic iron cycle will affect the utilization of the
- 630 added P. For example benthic denitrification is not simulated in the UVic model. Model simulations showed for this century, that the enhanced denitrification in the water column could be compensated by less benthic denitrification (Landolfi et al., 2017), which could reduce the N-limitation and therefore enhance the effect of P fluxes on the biological pump. Sources of bioavailable Fe are still not well quantified and how these sources change under climate change is under debate (Hutchins et al., 2016;
- 635 <u>Mahowald et al., 2005</u>). A more realistic representation of a dynamic iron cycle in UVic would affect <u>N2-fixation in many areas of the global ocean (Fig. 8).</u>

Some additional model limitations are a cause for uncertainty in our results. We considered a fixed Redfield-ratio stoichiometry. In future deoxygenation studies, an optimality-based model for nutrient uptake with variable nutrient ratios (Pahlow et al., 2013) could be applied to investigate how well

- 640 marine organisms adapt to a changing nutrient availability in the global ocean. Sea level change and the implied bathymetry change were not simulated in the UVic model. In future projections, higher surface air temperatures would lead to a rise in sea level, which increase global coverage of shelf areas. Burial of P is more effective on the shelf (Flögel et al., 2011), which would remove P from the ocean and lead to a lower marine P residence time (Bjerrum et al., 2006).
- 645 To conclude, climate warming leads to a larger oceanic P inventory mainly due to addition of P by weathering, but also due to the release of P from the sediment and due to anthropogenic fluxes. A realistic representation of shelf bathymetry improves the predicted benthic P fluxes. Transfer functions for benthic P release should consider the sedimentary P inventory. However, the largest uncertainties in the projection of oceanic P inventory are due to poorly constrained weathering fluxes of P. Although
- additional deoxygenation is driven by P addition to the ocean, the degree of deoxygenation and hence
   the positive redox-related feedback on benthic P <u>release</u> is eventually limited by the availability of N and the apparent inability of the modelled N<sub>2</sub> fixation to respond to the larger P inventory.

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**Data and Code Availability.** The model data and the model code are available at https://data.geomar.de/thredds/catalog/open\_access/kemena\_et\_al\_2018\_esd/catalog.html.

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Author contributions. All authors discussed the results and wrote the manuscript. T.P $\underbrace{K}$ . led the writing of the manuscript and the data analysis.

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Competing interests. The authors declare that they have no conflict of interest.

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Tables:

910Table 1: Overview of simulations. P fluxes are given in TmolP a<sup>-1</sup>. We divided all simulations in four groups<br/>indicated by different colors. These are: reference simulations (in black) with and without anthropogenic<br/>fluxes of P; simulations with different formulations for the burial (in red beginning with the acronym Bur);<br/>simulations with weathering fluxes of P for different climate sensitivities (in blue beginning with the<br/>acronym Weath); and simulations with different representations of the sediment (in purple). In the P<br/>weathering simulations, only weathering anomalies were applied. The weathering flux ( $W_{P,0}$ ) balances P<br/>burial (BUR<sub>P</sub>) during the spin-up simulations. The preindustrial P inventory is identical in all simulations.<br/>More detailed information can be found in the text.

Simulations	Abbreviation	Fluxes	P Burial parametrization	
Reference (constant P inv.)	Ref	No	No burial	
Anthropogenic P input	Anthr	Flux from Filippelli	No burial	
_		(2008)		
Burial Reference	Bur	BUR <sub>P</sub> (t=1775a)=0.38	<i>r</i> <sub>C:P</sub> (Wallmann, 2010),	<u> </u>
		$W_{P,const}=0.38$	C Burial (Flögel et al., 2011)	Tronje Kemena 28.2.2019 11:40
			<u><i>Y<sub>F</sub></i>=123; <i>A</i>=112; <i>r</i>=32 in Eq. 4</u>	Deleted: Weathering[1]
Burial Dunne	Bur_Dun	BUR <sub>P</sub> (t=1775a)=0.25	<i>r</i> <sub>C:P</sub> (Wallmann, 2010), C	
		$W_{P,const}=0.25$	Burial (Dunne et al., 2007)	
Low burial estimate	Bur_low	BUR <sub>P</sub> (t=1775a)=0.21	Bur configuration, but with	
		$W_{P,const}=0.21$	<i>Y<sub>F</sub></i> =100.5; <i>A</i> =90; <i>r</i> =38 in <u>Eq. 4</u>	
High burial estimate	Bur_high	BUR <sub>P</sub> (t=1775a)=0.60	Bur configuration, but with	Tronje Kemena 28.2.2019 11:40
		$W_{P,const}=0.60$	$Y_F = 167; A = 108.5; r = 29.5 \text{ in } Eq.$	Deleted: (3)
			<u>4</u>	Tronje Kemena 28.2.2019 11:40
Burial without subgrid	Bur_noSG	<u>BUR<sub>P</sub> (t=1775a)=0.09</u>	Bur configuration, but without	Deleted: (3)
<u>bathymetry</u>		$\underline{W}_{P,const}=0.09$	subgrid bathymetry	
Burial with restricted	Bur_res	BUR <sub>P</sub> (t=1775a)=0.41	Bur configuration, but with 113	
reservoir		$W_{P,const}=0.41$	µmolP cm <sup>-2</sup> Reservoir	Tronje Kemena 28.2.2019 11:40
Weathering	Weath0.05	$W_{P,p}=0.05$	No burial	<b>Formatted:</b> Font color: Custom Color(RGB(252;0;235))
Weathering	Weath0.10	<u>W<sub>P,0</sub>=0.10</u>	<u>No burial</u>	Tronje Kemena 28.2.2019 11:40
Weathering	Weath0.15	$W_{P,0} = 0.15$	No burial	Deleted: Burial without subgrid bathymetry
Weathering	Weath0.38	$W_{P,0} = 0.38$	No burial	Tronje Kemena 28.2.2019 11:40
	l	1		Formatted Table Tronje Kemena 28.2.2019 11:40
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 BUR<sub>P</sub> (t=1775a)=0.09

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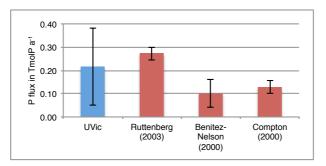
Tronje Kemena 28.2.2019 11:40

Tronje Kemena 28.2.2019 11:40 **Deleted:** *Bur* configuration, but without subgrid Table 2: Rain rate of particulate organic carbon  $(RR_C)$  to the seafloor for the shelf, slope and deep-sea areas from the observational estimate by Bohlen et al. (2012) and for the UVic model simulation *Bur* with and without subgrid bathymetry. Preindustrial RR<sub>C</sub> shows no significant differences among all model simulations (expect for simulation *Bur\_noSG*).

		Bohlen (2012)			UVic model with subgrid bath. (Simulation <i>Bur</i> )		UVic model without subgrid bath. (Simulation <i>Bur_noSG</i> )			
	Depth	RR <sub>C</sub>	RR <sub>C</sub>	Area	RR <sub>C</sub>	RR <sub>C</sub>	Area	RR <sub>C</sub>	RR <sub>C</sub>	Area
	[ <b>m</b> ]	[TgC a <sup>-1</sup> ]	[%]	[%]	[TgC a <sup>-1</sup> ]	[%]	[%]	[TgC a <sup>-1</sup> ]	[%]	[%]
Shelf	0-200	1056	60	6	1039	70	6.5	179	28	2.3
Slope	200-2000	393	22	10	205	14	11.7	219	34	13.3
Deep sea	>2000	312	18	84	235	16	81.9	238	37	84.6
Sum		1761			1479			637		

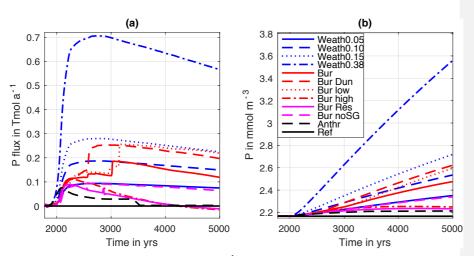
# Figures:

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Fig. 1: Globally integrated preindustrial P weathering fluxes in TmolP a<sup>-1</sup> from field studies(red) and the range of preindustrial P weathering fluxes covered by all simulations (blue with bars indicating the range; see W<sub>P,0</sub> in Table 1). Estimates from field studies are based on literature values for global fluvial fluxes of bioavailable P and the error bars denote upper and lower limits of these estimates.



950 Fig. 2: (a) Globally integrated flux of P in Tmol a<sup>-1</sup> to the ocean and (b) globally averaged phosphate concentration in mmol m<sup>-3</sup>. Simulation descriptions can be found in Table 1.

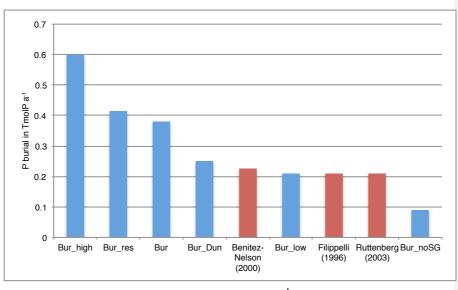


Fig. 3: Globally integrated preindustrial P burial fluxes in TmolP a<sup>-1</sup> from field studies (red) and for UVic model simulations in <u>the</u> year 1775 (blue). Description of the model simulations can be found in Table 1.



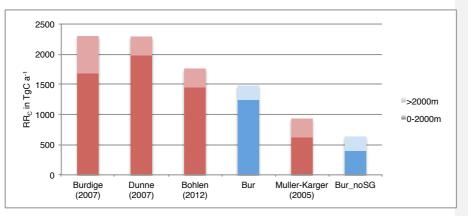
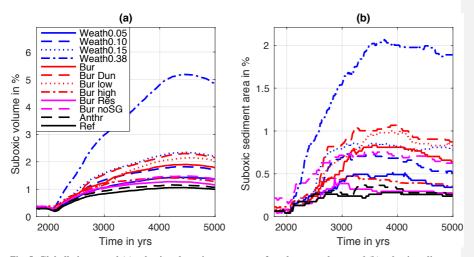
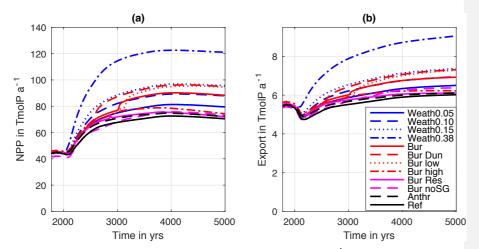


Fig. 4: Globally integrated preindustrial rain rate of particulate organic carbon  $(RR_c)$  to the seafloor in TmolC a<sup>-1</sup> from published studies (red) and for UVic model simulations (blue) between 0 to 2000m water depth (dark blue) and below 2000m (light blue). The simulation *Bur* is representative for all UVic model simulations except *Bur\_noSG*.

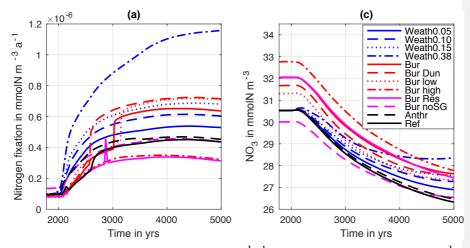


965 Fig. 5: Globally integrated (a) suboxic volume in percentage of total ocean volume and (b) suboxic sediment surface area in percentage of total sediment surface area. Water is designated as suboxic for oxygen concentrations below 5 mmolO<sub>2</sub> m<sup>-3</sup>. Simulation descriptions can be found in Table 1.

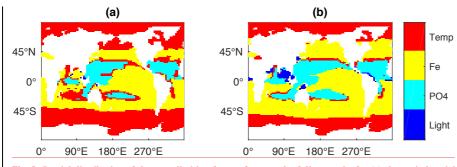


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Fig. 6: Globally integrated (a) ocean net primary production (NPP) in TmolP a<sup>-1</sup> and (b) export of organic P below the 130m depth level in TmolP a<sup>-1</sup>. Simulation descriptions can be found in Table 1.

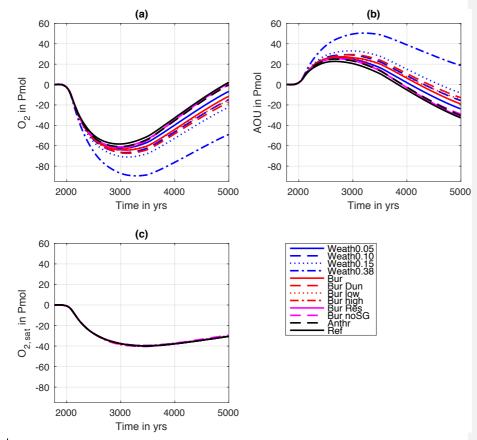


975 Fig. 7: Globally averaged (a) N<sub>2</sub>-fixation in mmolN m<sup>-3</sup> a<sup>-1</sup> and (b) NO<sub>3</sub><sup>-</sup> concentration in mmolN m<sup>-3</sup>. Simulation descriptions can be found in Table 1.



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Fig. 8: Spatial distribution of the most limiting factors for growth of diazotrophs for (a) the preindustrial case and (b) simulation year 5000 for *Weath0.15*. Limitation of iron (Fe) and phosphate (PO4) are based on Monod kinetics so that the limitation factors vary between 0 and 1. The light limitation factor also varies between 0 and 1. In the model, diazotrophs only grow at temperatures higher than 15.7 °C. For temperatures above 15.7 °C, diazotroph growth depends on the equation exp(T/15.7°C)-2.61. Diazotroph growth is not limited by nitrate availability in the model. A more detailed description of diazotroph growth and iron limitation can be found in Keller et al. (2012) and Nickelsen et al. (2015).



990 Fig. 2: Anomalies of globally integrated (a) O<sub>2</sub> content, (b) apparent oxygen utilization (AOU) and (c) oxygen saturation (O<sub>2,sat</sub>) in Pmol O<sub>2</sub>. Simulation descriptions can be found in Table 1.

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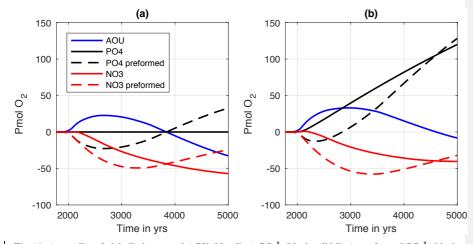


Fig. <u>10</u>: Anomalies of globally integrated AOU (blue line),  $PO_4^{3-}$  (black solid line), preformed  $PO_4^{3-}$  (black dashed line),  $NO_3^{-}$  (red solid line) and preformed  $NO_3^{-}$  (red dashed line) expressed in Pmol O<sub>2</sub> equivalents using constant elemental ratios (O:N=10 and O:P=160) for the (a) *Ref* simulation and the (b) *Weath0.15* simulation. Preformed nutrients are calculated as the difference between remineralized and total nutrient content. The calculations assume that all ocean water <u>leave</u> the surface layer saturated in O<sub>2</sub>.

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