Responses to Reviewer#1

We would like to thank the reviewer for their time and expertise. We have replied and acted on all their thoughtful and constructive comments and advice (Reviewer's comments in blue).

General comments

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This is an interesting paper on coupled phosphorus and oxygen dynamics in the modern ocean essentially showing that both weathering and, to a lesser extent, a phosphorus-oxygen feedback, can contribute to expanding anoxia on a time scale of 1000 kyrs. While the results are important and definitely deserve publication, there are a number of issues that I recommend the authors consider in a revision, as detailed below.

Major issues:

1. The context could be more clearly presented. The point is that you wouldn't really expect a major impact of P recycling on global ocean biogeochemistry (apart from the coastal zone) on time scales of 1000 kyrs given the relatively long residence time of P in the ocean. In this paper, changes in the modern day ocean under climate change on time scales of 1000 years are repeatedly even compared directly to changes in the Cretaceous Ocean that acted on time scales of 100.000 years and more in an ocean with a very different configuration (other paleogeography, higher sea level, larger coastal zone). This direct comparison is not recommended: the temporal and spatial scales were just too different. More careful phrasing is thus needed. Furthermore, various recent studies of Cretaceous biogeochemistry suggest that both weathering and recycling of P were needed to sustain the oceanic anoxia (e.g. see the work of Ruvalcaba et al. published in BG in 2014 and the work of Monteiro in GBC).

Thank you very much for your advice. We agree with you and will rephrase in the manuscript in a more careful manner and skip the direct comparisons with the Cretaceous.

The referencing needs more attention. There are three issues: results of quite some key papers are missing (e.g. relevant to river P fluxes, modeling for the Cretaceous, etc., see below), not all references in the text are in the reference list (see below) and it's strange to cite a thesis when the same work has already been published in the peer-reviewed literature. (work of Tsandev).

Thank you. We will carefully edit the referencing, correct the citation of Tsandev and add some key references (RUTTENBERG (2004); TYRELL (1999); RUVALCABA BARONI ET AL. (2014); SLOMP (2011)).

- 30 3. The writing style can be improved. There are words missing and there are several awkward and/or unclear formulations.
 - We apologize for the writing style of the manuscript. We revised it carefully according to imprecise formulations as well as incomplete sentences. In addition, the revised paper was now proof-read by a native speaker.
 - 4. Many key issues, such as the role of the coastal zone (in what detail is it included in this model), the bathymetry, the role of anthropogenic fluxes of nutrients (are they considered?) etc. are discussed only at the end of the paper in a section

"uncertainties". It would be much better to address these issues up front in the introduction and/or as assumptions in the model description sections.

Thank you. We will add a section about bathymetry and coastal margins in the model description. Although the discussion of these aspects is important, they cannot be fully resolved in this coarse-resolution pilot study. We address these issues together with those of anthropogenic nutrients in section 4 'Uncertainties'. In addition, we now mention in the introduction,

that these issues will need more attention in follow-up studies.

5. The river fluxes assumed in the model are critical to the results but the river fluxes from the literature discussed seem to be selected rather arbitrarily. I miss references to the work of Ruttenberg (2004; Treatise of Geochemistry), for example. Further details are provided below.

We will include the comprehensive summary of P fluxes by RUTTENBERG (2004). As she reports higher P fluxes to the ocean, our results are in relatively good agreement with fluxes from the literature.

Page 1. Line 9: replace "reduced solubility" by "reduced oxygen solubility"

Corrected.

Page 1. Line 13: replace "Higher availability in phosphorus" by "A higher availability of phosphorus"

15 Corrected.

Page 1. Line 16: the last part of the sentence is repetitive and can be removed, i.e. "which in turn, got there through weathering".

Corrected.

Page 1. Lines 19-21. The use of "although" in this sentence suggests that the finding here for the OMZ somehow contrasts with the findings described for the Cretaceous. However, the direct comparison of the impact of the benthic phosphorus release feedback on the size of the OMZ over the coming 1000 years to the feedback on anoxia in the Cretaceous ocean is not appropriate. This is because the relevant processes in the Cretaceous ocean acted on time scales of more than 100,000 years, i.e. there is a 3-order of magnitude difference in time scale.

Thank you for your careful reading. We corrected the sentence. In the revised manuscript the misleading direct comparison

25 has been removed.

Page 1. Line 21. Previous studies do not "assume" that the P feedback "was the main factor for anoxic conditions during Cretaceous period". They show that both increased river inputs and enhanced regeneration of P likely played a role.

Corrected.

Page 2 Lines 3-4. Sentence is too long. Please break up into two sentences.

30 Corrected.

Line 4. Stramma et al. (2012) and Cabre et al. (2015) are not in the reference list.

Corrected.

Line 11. A reference to Tyrell (1999; Nature) would be appropriate here.

The reference will be added.

Line 13. Change to "is river input"

Corrected.

Line 18. Specify that you are using the pre-anthropogenic flux of P from rivers.

Thank you for this suggestion to clarify the presentation. We will add this specification.

5 Lines 18-20. Why are the data of Ruttenberg (2004; Treatise of Geochemistry) not used here? That is the most comprehensive summary of reactive and total P fluxes in the marine environment, including river input. Importantly, she reports higher fluxes of P to the marine environment.

Thank you for this suggestion. A comparison to the data by RUTTENBERG (2004) will be added.

Page 3 Lines 8-10. Add references for these statements.

10 We will add the references of SABINE ET AL. (2004) and SARMIENTO & ORR (1991) for these statements.

Line 11. Change "in previous studies" by "in a previous study".

Corrected.

Lines 17-19. Rephrase. It is not correct to refer to Cretaceous studies as "Other studies on OMZs" since in many cases there was not an OMZ but the water column was anoxic to the seafloor also in the deep sea.

15 We apologize for the imprecise formulation used in this case. We will rephrase as follows:

'Other studies on marine oxygen deficiency focused on the geological past, especially the mid-Cretaceous warm period (120-80 Ma ago) (TSANDEV & SLOMP, 2009; HANDOH & LENTON, 2003; BJERRUM ET AL., 2006; FÖLLMI ET AL., 1996).'

Line 23. The Cretaceous work by Tsandev et al. was published in EPSL in 2009 – that paper should be referenced, not the PhD-thesis.

20 Corrected.

Line 23. I miss a reference to the modeling paper of Ruvalcaba et al. (2014; Biogeosciences) here.

Thank you for pointing out this additional reference. We will add the paper of RUVALCABA ET AL. (2014) in the revised manuscript.

Page 4. Section 2.1. I miss details on the bathymetry and how the model deals with coastal processes here.

- Thank you for your suggestion. We used a sub-grid bathymetry as described in SOMES ET AL. (2013) where smaller-scale (1/5°) features of continental shelves, slopes and other topographical features are included in the computation of biogeochemical fluxes. This favours a relatively precise illustration of benthic burial as well as benthic release, which are with regard to our study the most important coastal processes. We will add a description of this approach to the suggested section about bathymetry and coastal processes.
- 30 Line 17. Change to "the following equations"

Corrected.

Page 5. How do P burial fluxes calculated in this manner compare to actual P burial fluxes in the ocean per m² and per time?

Thank your for your helpful question. We calculated a burial rate of 1.068 mmol m⁻² a⁻¹ in our model. This burial rate is at the upper bound, but still in relatively good agreement with the range reported by RUTTENBERG (2004), who estimated a burial rate of 0.192-0.353 Tmol P a⁻¹ (=0.532-0.978 mmol m⁻² a⁻¹). We will add this comparison to our revised manuscript.

Page 6. Line 4. So is burial of P also excluded in this simulation? If so, this should be mentioned specifically ("benthic fluxes" is not generally assumed to refer to burial).

We apologize for this misunderstanding; we expressed ourselves in a misleading way. The second simulation includes weathering input, benthic release as well as benthic burial. We used benthic fluxes as an umbrella term for benthic burial and benthic release. In the revised manuscript we will change the wording to:

'The second simulation, called WB, includes P weathering as well as benthic burial and release of P but excludes additional anthropogenic input. The spin up was performed by computing the burial and benthic release according to Eq. 6.'

Page 6. Line 5. And burial of P? (see previous point).

Corrected (see previous point).

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Page 6. Line 5. Change to "was performed"

We think our expression is correct.

'Two model simulations were performed.'

Page 6. Line 6. What about anthropogenic inputs of P?

Thank you for this important question. In comparison to maximum weathering values computed here, the anthropogenic impact is small and was therefore not included in our simulations. This issue is briefly discussed in the discussion section, and we have also now included a statement in the description of the model simulations.

Page 6. Line 19 and further. Here, it is important to distinguish between burial rates for the open ocean and coastal zone. Palastanga et al. used a coarse resolution model that did not resolve the coastal zone and the burial flux thus refers to the open ocean.

Thank you for this important comment. In our study the calculated burial rate for the continental margins (0-200 m) is 0.334 Tmol P a⁻¹ and for the open ocean (>200 m) 0.046 Tmol P a⁻¹. Our estimate is in line with findings presented by RUTTENBERG (2004) and SLOMP (2011). This will be clarified in the revised manuscript.

Page 6. Note total fluxes of P to the ocean in the published have also been summarized by Ruttenberg (2004; Treatise of Geochemistry) and Slomp (2011; Treatise on Coastal and Estuarine Science) with estimates ranging from 0.258 to 0.92 Tmol yr⁻¹. Part of this total P can indeed by mobilized (i.e. become soluble) in the coastal zone and it is well-known that river fluxes of dissolved P fluxes to the ocean thus underestimate P inputs. Thus there are significantly more data available than suggested here.

Thank you for your advice. We will add the suggested references in the revised manuscript.

Page 7. Lines 1-4: where is the P buried in the current model, i.e. how much is buried in the coastal zone and how much is buried in the open ocean? Again, comparisons should be done carefully: the Palastanga et al. estimates refer to the open ocean because the coastal zone is not well-resolved.

Thank your for your comment. We agree that a distinction between coastal margin and open ocean is important with regard to benthic burial and benthic release. We will include a comparison with the data compilation by RUTTENBERG (2004) and calculate the benthic release as well as benthic burial in UVic ESCM for continental margins and for the open ocean to compare them with previous studies.

5 Page 7. Lines 16-17. I would remove this here; because you are pointing forward and are not explaining this fully, it doesn't really fit.

Corrected.

Page 7. Lines 23-24. Where can I see that benthic burial acts as a P sink?

The marine phosphorus inventory in our model is determined by continental inputs through P weathering as the only source and burial at the seafloor as the only the sink of P in the ocean. In order to illustrate this further we will add a figure regarding benthic burial in the supplement (see Figure S1 and below).

Page 8. Lines 11-13. Please show the results for P burial (if you don't want them in the main paper, add them in a supplement).

We will add P burial results in the supplement (see Figure S1 and below).

15 Page 8. Line 17. Please show these results (see above).

Please see our supplement, where we have now added a figure showing benthic release (see Figure S1 and below).

Page 8 Line 18: I would suggest to remove "also"

Corrected.

Page 8. Line 27: explain:"unlimited"

We apologise for this imprecise formulation. The benthic release is calculated by subtracting the benthic burial from the particulate organic P rain ratio (see Equation 7). In our simulations the rain ratio shows a strong increase, while the benthic burial is decreasing resulting in an increase of benthic release. Of course, benthic release is limited by the particulate organic P rain ratio. We have removed the term 'unlimited' in the new version.

Page 8. Lines 28-30: what about the coastal regions?

We agree that the coastal margins are very important. From year 1775 until 10,000 the suboxic volume in the coastal margins increases by about a factor 50 ($O_{2_{-1775}} = 0.12\%$ of total coastal region; $O_{2_{-10000}} = 5.57\%$) in the WB-simulation. A maximum increase of 7.29% is simulated from 4785 until 4805, which is still too low for widespread anoxia in coastal regions.

Page 8: Lines 29-30. Show the result for the 10000-year simulation (e.g. in a supplement)

We will add results for the 10,000-year simulation to the supplement (see Figure S1 and S2 and below).

Page 9. Lines 16-17: Based on the residence time of P in the ocean, I wouldn't expect run-away anoxia on a time scale of 1000 years to start with.

Thank you for your suggestion. We will reformulate this part.

Page 9. Lines 18-19. Adding "as has been suggested during the Cretaceous" is inappropriate because the processes at the time occurred at a different time scale, thus, a direct comparison should not be made. Note also that we know for certain that parts of the ocean (the proto-North Atlantic) were anoxic in the Cretaceous.

We apologise for the inappropriate statement. As already mentioned above we will skip the direct comparison to the

5 Cretaceous and reformulate this section more carefully.

Page 9. Line 19. Tsandev et al. 2009; EPSL is the right reference. It would also be logical to discuss the Monteiro et al. and Ruvalcaba- Baroni et al. results here, if you want to discuss modeling results for the Cretaceous. See earlier comment.

Thank you for your advice. Instead of discussing modelling results for the Cretaceous, we decided to keep the focus on our own results. Therefore we removed that paragraph.

Page 9: 21-23. I would also add: "present-day paleogeography" because the latter factor also played a role in Cretaceous nutrient cycling.

Thank you for your careful reading. We changed the expression to present-day bathymetry and geography.

Page 9. The cause of the "unlimited P reservoir" could be better explained, see earlier comment.

Please see comment above.

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15 Page 10. Lines 1-3: It would be better to describe up front in the model how well the coastal zone is resolved and use that information when discussing results and the parameterization (e.g. burial of P and benthic fluxes, see earlier comment).

We agree with the reviewer. As already mentioned earlier we now add a short discussion of benthic burial and release in section 'Uncertainties' as well as a description in section 2.1 'UVic Model'.

Page 10. Lines 14-19. The potential role of anthropogenic inputs of P to the ocean is better discussed in the model description section, especially because anthropogenic CO₂ inputs are considered. Is there not more recent work on anthropogenic inputs of P to the ocean that is relevant to include here, e.g. from the Global NEWS project? (e.g. Harrison et al., Beusen et al. etc.).

We apologise for this misunderstanding. In our simulation we assume only enhanced weathering rates under climate change conditions, thus we exclude additional anthropogenic inputs into the ocean. We will clarify this in the revised version of the manuscript.

Page 10. Lines 29-32. This feedback is not explained well.

Thank you for pointing this out. We assume an increasing P weathering rate, which enhances the ONPP and the detritus export into the deep ocean. This in turn can lead to an increase in marine uptake of atmospheric CO_2 , which will impact surface air temperature through a negative feedback loop resulting in a decrease in continental P weathering input. We will clarify the explanation of the feedback in the introduction.

Figure 2: Please improve the readibility of this figure by adding legends in the panels and/or other markers. It takes a lot of time for the reader to figure out what is what.

This is a very good idea. We will improve the readability of the mentioned figure by adding legends in the panels (see Figure 2 in revised manuscript and below).

Figures:

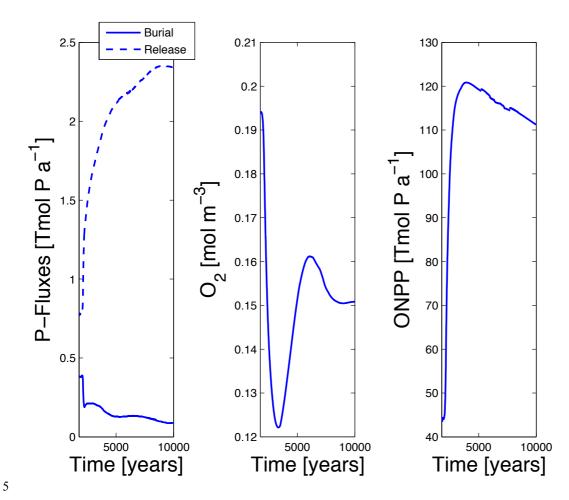


Figure S 1: Global mean and annual mean time series of phosphorus burial (blue solid line; left), phosphorus release (blue dashed line; left) and oxygen (blue solid line; right) for simulation WB until year 10,000.

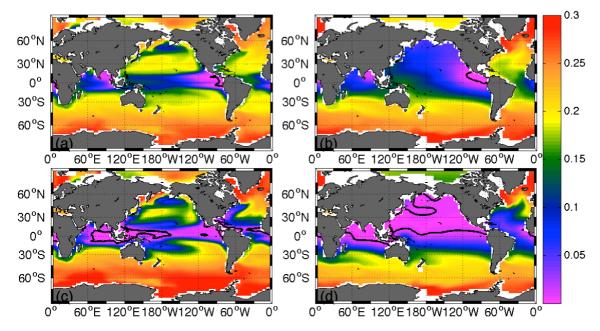


Figure S 2: Oxygen concentration in mol O_2 m⁻³ at year 10,000 simulated by the (a) control simulation at 300m depth, (b) and 900m depth, (c) simulation WB at 300m depth and (d) simulation WB at 900 m depth. The black contour lines at 0.005 mol m⁻³ highlight the oxygen minimum zones (OMZs).

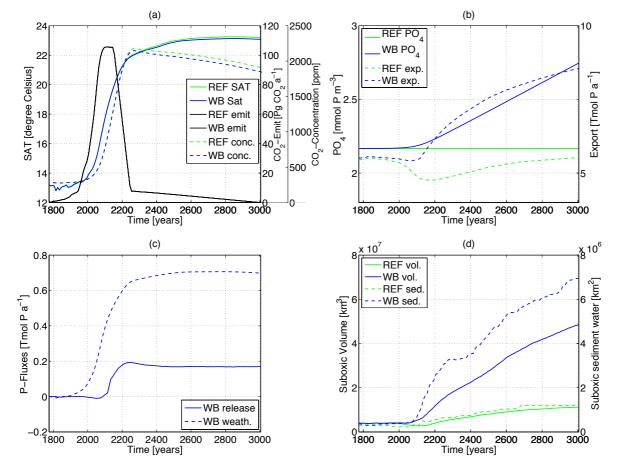


Figure 2: Global and annual mean time series of (a) Surface Air Temperature in degree Celsius (solid lines), CO₂-emissions in Pg CO₂ a⁻¹ (black solid line (for both simulations)) and CO₂-concentration in ppm (dashed lines); (b) phosphorus concentration in mmol P m⁻³ (solid lines) and export rate in Tmol P a⁻¹ at 130 m depth (dashed lines); (c) anomalies of phosphorus input via sediment in Tmol P a⁻¹ (solid line) and anomalies of phosphorus weathering input in Tmol P a⁻¹ (dashed line); (d) suboxic volume (<0.005 mol m⁻³) of the ocean in km³ (solid lines) and surface of ocean bottom layer with O₂ concentrations below 0.005 mol m⁻³ (dashed lines). The control simulation (REF) is shown in green, simulation WB in blue.

Responses to Reviewer#2

We would like to thank the reviewer for their time and expertise. We have replied and acted on all their thoughtful and constructive comments and advice (Reviewer's comments in blue).

Using the UVic Earth System Model the authors describe a feedback loop between expanding oxygen minimum zones (OMZ's) and the availability of dissolved inorganic phosphorus (DIP). A warming climate stimulates weathering processes on land leading to an eutrophication of the oceans. The excess nutrients are taken up by marine phytoplankton which decays due to bacterial decomposition while it sinks out of the euphotic zone, thereby consuming extra oxygen. Increasing benthic oxygen depletion stimulates the redox dependent phosphorus fluxes from sediments, further elevating the concentration levels of DIP, leading to an even larger spread of OMZ's.

General comments:

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The paper provides an interesting contribution to the actual discussion of the trends of oxygen concentrations under the impact of anthropogenic green house gas emissions. It discusses at the first time the very relevant issue of the threat of an accelerated expansion of OMZ's due to a warming- induced phosphorus-oxygen feedback. The paper is nicely written and I recommend it - subject to minor revisions - for publication in the journal "Earth System Dynamics".

Specific comments

- The authors report an increase of ocean net primary production (ONPP) between preindustrial times and year 3005 from 43.8 Tmol P a⁻¹ to 65 Tmol P a⁻¹ even for their reference model run (REF). Usually, global warming is thought to cause a decline in chlorophyll_a concentrations and NPP owing to a strengthening of ocean stratification (see references below).

 Gregg W W, Casey N W and McClain C R 2005 Recent trends in global ocean chlorophyll Geophys. Res. Lett. 32 L03606 Boyce D G, Lewis M R and Worm B 2010 Global phytoplankton decline over the past century Nature 466 591–6
- 25 The authors should provide a short discussion of how this increase in ONPP, notably in the tropical ocean of their model, can be explained.

Thank you for this very important comment. In the revised version of the manuscript we will add a discussion about processes altering ONPP under climate change projection as the correlation between temperature and ONPP is still unclear. GREGG ET AL. (2005) and BOYCE ET AL. (2010) suggest a decrease of ONPP under climate change conditions based on enhanced stratification. However, SARMIENTO ET AL. (2004) argued that the temperature sensitivity of ONPP could be the main cause for an increase in ONPP. TAUCHER & OSCHLIES (2011) also highlighted in their study with the UVic-ESCM that simulated future changes in ONPP are very sensitive to the assumed temperature effects on metabolic rates. Furthermore, KVALE ET AL. (2015) found a near-linear relationship between both parameters. Consequently, it can be assumed that the direction of ONPP change depends on the strength of temperature effect versus stratification effect. In our model the direct

effect of temperature on metabolic rates overcompensates the stratification effect and thus leads to a net increase in ONPP under global warming.

The volume of OMZ's in UVic under present day conditions is drastically underestimated in comparison with observational data (15.8x10⁶ km³ vs. 102x10⁶ km³). The authors should discuss this flaw more in detail, notably if and how it could influence their conclusions. I would like to see the oxygen concentration map not only in 300 m depth (as shown in Figure 5) but also at depth of 900 m.

Because of still relatively poor data coverage and heavy reliance on inter- and extrapolation routines, the data-based estimates for the volumes of OMZs vary widely and the definitions are not yet uniform. Using 20 mmol m⁻³ as threshold for OMZs and comparing our results (WB₂₀₀₅ = 1.58*10⁷ km³) with results of the WOA (WOA₂₀₀₅=4.12*10⁵ km³), PAULMIER ET AL. (Paulmier₂₀₀₉ = 102*106 ± 15*10⁶ km³) or BIANCHI ET AL. (Bianchi₂₀₁₂ = 2.28-2.78*10⁶ km³) it seems that the volume of OMZs are difficult to validate. Our result is within the wide range of these estimates. Looking at the feedbacks described in the manuscript, the suboxic sediment area is more important for the benthic release feedback than the suboxic volume in the water column, which does not necessarily reach the seafloor. In our study we calculated a suboxic sediment area of WB₂₀₀₅ = 3.8*10⁵ km², which fits well with data of the WOA₂₀₀₅ = 2.48*10⁵ km². We will add this discussion to our revised manuscript.

We have also added an oxygen concentration map at a depth of 900 m to the supplement (see Figure S3 and below).

Technical corrections

In the abstract the sentence ending with: " ... due to increased alkalinity, which, in turn, got there through weathering." sounds awkward. Please rephrase.

20 Corrected.

Page 6 line 19 please replace Tol P a⁻¹ by Tmol P a⁻¹

Corrected.

Figures:

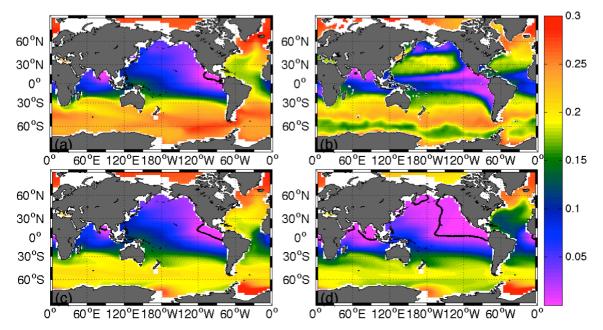


Figure S 3: Oxygen concentration in mol O_2 m⁻³ at 900m depth simulated by the (a) control simulation at year 1775 (representative for both REF and WB model runs in year 1775), (b) the World Ocean Atlas in 2009, (c) the control simulation at year 3005 and (d) simulation WB at year 3005. The black contour lines at 0.005 mol m⁻³ highlight the oxygen minimum zones (OMZs).

A model study of warming-induced phosphorus-oxygen feedbacks in open-ocean oxygen minimum zones on millennial timescales

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Abstract. Observations indicate an expansion of oxygen minimum zones (OMZs) over the past 50 years, likely related to ongoing deoxygenation caused by reduced oxygen solubility, changes in stratification and circulation, and a potential acceleration of organic matter turnover in a warming climate. The overall area of ocean sediments that are in direct contact with low oxygen bottom waters also increases with expanding OMZs. This leads to a release of phosphorus from ocean sediments. If anthropogenic carbon dioxide emissions continue unabated, higher temperatures will cause enhanced weathering on land, which, in turn, will increase the phosphorus and alkalinity fluxes into the ocean and therefore raise the ocean's phosphorus inventory even further. A higher availability of phosphorus enhances biological production, remineralisation and oxygen consumption, and might therefore lead to further expansions of OMZs, representing a positive feedback. A negative feedback arises from the enhanced productivity-induced drawdown of carbon and also increased uptake of CO₂ due to weathering-induced alkalinity input. This feedback leads to a decrease in atmospheric CO₂ and weathering rates. Here we quantify these two competing feedbacks on millennial timescales for a high CO₂ emission scenario. Using the UVic Earth System Climate Model of intermediate complexity, our model results suggest that the positive benthic phosphorus release feedback has only a minor impact on the size of OMZs in the next 1000 years. The increase in the marine phosphorus inventory under assumed business-as-usual global warming conditions originates, on millennial timescales, almost exclusively (>80%) from the input via terrestrial weathering and causes a 4 to 5-fold expansion of the suboxic water volume in the model.

1 Introduction

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Oxygen minimum zones (OMZs) have more than quadrupled over the past 50 years and it has been suggested that this expansion is related to recent climate change (STRAMMA ET AL., 2008; SCHMIDTKO ET AL., 2017). However, current CO₂ emission-forced models are challenged to reproduce this expansion in detail (STRAMMA ET AL., 2012; CABRE ET AL., 2015). There are at least three different processes that can have an impact on the size of OMZs in a warming climate: ocean warming and its impact on solubility of O₂ in the ocean (BOPP ET AL., 2002), changes in ocean dynamics, e.g. stratification, convective mixing and circulation (MANABE & STOUFFER, 1993; SARMIENTO ET AL., 1998), biological production effects (BOPP ET AL., 2002) including possible CO₂-driven changes in stoichiometry (OSCHLIES ET AL., 2008) and CO₂ induced changes in ballasting particle export (HOFMANN & SCHELLNHUBER, 2010). Here we investigate how changes in biological production and subsequent remineralisation can affect OMZs in addition to the above-mentioned thermal and dynamic 10 effects. We focus on changes in the phosphorus (P) cycle. P is the main limiting nutrient on long timescales (TYRELL, 1999; PALASTANGA ET AL., 2011) and we examine possible effects of changes in the P cycle on millennial timescales. The major source of P for the ocean is river input (FILIPPELLI, 2008; PAYTON & MCLOUGHLIN, 2007; FÖLLMI, 1996, PALASTANGA ET AL., 2011; FROELICH ET AL., 1982), which is determined by terrestrial weathering of apatite (FILIPPELLI, 2002; FÖLLMI, 1996). The main factors controlling terrestrial weathering are temperature, precipitation and vegetation. Higher temperatures are generally associated with enhanced precipitation and in many places with higher terrestrial net primary productivity (MONTEIRO ET AL., 2012), which all tend to increase weathering rates (BERNER, 1991). It is difficult to determine how much of the globally weathered P enters the ocean in a bioavailable form. Today, about 0.09 -0.15 Tmol a⁻¹ of prehuman, potentially bioavailable P is transported globally by rivers including dissolved organic and inorganic P, particulate organic P and ironbound P (COMPTON ET AL., 2000). About 25% of this potentially bioavailable P is trapped in coastal estuaries and will not enter the open ocean (COMPTON ET AL., 2000). RUTTENBERG (2004) estimated a bioavailable P flux under preindustrial conditions including dissolved P and bioavailable particulate P (=35% of total particulate P) of 0.24-0.29 Tmol P a⁻¹ excluding the atmospheric input (RUTTENBERG, 2004). Marine organisms take up P most easily as dissolved inorganic P (DIP). Riverine measurements suggest that only a small fraction of the total P (0.012 to 0.032 Tmol a⁻¹) enters the ocean as DIP (FILIPPELLI, 2002; HARRISON ET AL., 2005;

COMPTON ET AL., 2000; WALLMANN, 2010; PALASTANGA ET AL., 2011; RUTTENBERG, 2004). However, passing through estuaries can increase the fraction of DIP by 50% (FROELICH, 1984) to 80% (BERNER & RAO, 1994).

After taking up the bioavailable P for photosynthetic production of biomass, a large fraction of the newly produced organic matter is exported out of the euphotic zone as detritus (6.42 Tmol P a⁻¹ according to the model study by PALASTANGA ET AL., 2011) and the vast majority of this exported organic matter is remineralised in the deeper ocean by bacteria (6.26 Tmol P a⁻¹; PALASTANGA ET AL., 2011), which is an oxygen consuming process. A small fraction of the exported organic matter is deposited at the sediment surface (0.16 Tmol P a⁻¹; PALASTANGA ET AL., 2011), about 20% of the deposited P is buried in the sediments on long time scales (0.032 Tmol P a⁻¹; PALASTANGA ET AL., 2011) and the remaining 80% (0.13 Tmol P a⁻¹; PALASTANGA ET AL., 2011) is released back into the water column as DIP, where it is again available for the uptake of marine primary producers (PALASTANGA ET AL., 2011; WALLMANN, 2010).

The processes of burial and release of P are redox-dependent. Under oxic conditions the burial rate is high, while under suboxic conditions the benthic release of P is elevated (INGALL & JAHNKE, 1994; KRAAL ET AL., 2012; WALLMANN, 2010; SLOMP & VAN CAPPELLEN, 2007; FLOEGEL ET AL., 2011; LENTON & WATSON, 2000; TSANDEV & SLOMP, 2009). The redox-dependent release of P into the water column and the decrease in marine oxygen due to remineralisation therefore represent a positive feedback loop on marine biological production (see Fig. 1). Although the feedbacks between ocean and atmosphere are complex (SABINE ET AL., 2004), we assume that an enhanced detritus export into the ocean interior results in an increased marine uptake of atmospheric CO₂ (SARMIENTO & ORR, 1991). Consequently, surface air temperatures decrease with decreasing atmospheric CO₂ concentrations, which, in turn, leads to lower weathering rates (see Fig. 1).

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These redox-dependent benthic P fluxes have been investigated in a previous study with the HAMOCC global ocean biogeochemistry model by PALASTANGA ET AL. (2011). PALASTANGA ET AL. (2011) show that doubling the input of dissolved P from rivers results in an increased benthic release of P. This leads to a rise in primary production as well as in oxygen consumption, which in turn affects the oxygen availability in sediments. The benthic release of P acts therefore as a positive feedback on expanding oxygen minimum zones on timescales of 10,000 to 100,000 years (PALASTANGA ET AL., 2011).

Other studies on marine oxygen deficiency focused on the geological past, especially the mid-Cretaceous warm period (120-80 Ma ago) (TSANDEV & SLOMP, 2009; HANDOH & LENTON, 2003; BJERRUM ET AL., 2006; FÖLLMI ET AL., 1996). Several periods of oceanic oxygen depletion have been inferred from sediment data of black shales (SCHLANGER & JENKYNS, 1976)—for example for the Cretaceous oceanic anoxic event 2 (OAE) at the Cenomanian-Turonian boundary (93.5 Myrs). Whether processes such as surface warming, sea-level rise (HANDOH & LENTON, 2003), and possibly a slow-down of the ocean overturning circulation and vertical mixing (MONTEIRO ET AL., 2012; TSANDEV & SLOMP, 2009; RUVALCABA BARONI ET AL., 2014) - as assumed for the Cretaceous - will lead to widespread oxygen depletion in the future, is a reason of concern. Consequently, a better understanding of biogeochemical processes associated with Cretaceous OAE might help assess the risk of possible future events of low marine oxygen concentrations (TSANDEV & SLOMP, 2009).

In contrast to previous studies that focus on the geological past, we investigate possible future changes over the next 1000 years using an Earth System Climate Model of intermediate complexity to investigate the feedbacks between the P cycle and OMZs under the extended Representative Concentration Pathways-Scenario 8.5 (RCP 8.5) of the Intergovernmental Panel on Climate Change (IPCC) AR5 report. The RCP 8.5 scenario is characterised by an increase in atmospheric CO₂ concentrations and associated with an increase in radiative forcing of up to 8.5 W m⁻² by year 2100 (in comparison to preindustrial conditions) and is also known as the "business as usual" scenario (RIAHI ET AL., 2011).

2 Methods

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2.1 UVic Model

The University of Victoria Earth System Climate Model (UVic ESCM) version 2.9 (WEAVER ET AL., 2001; EBY ET AL., 2009) is a model of intermediate complexity and consists of a terrestrial model based on TRIFFID and MOSES (MEISSNER ET AL., 2003) including weathering (MEISSNER ET AL., 2012), an atmospheric energy-moisture-balance model (FANNING & WEAVER, 1996), a CaCO₃-sediment model (ARCHER, 1996), a sea-ice model (SEMTNER, 1976; HIBLER, 1979; HUNKE & DUKOWICZ, 1997) and a three-dimensional ocean circulation model (MOM2) (PACANOWSKI, 1995). The ocean model includes a marine ecosystem model based on a nutrient-phytoplankton-zooplankton-detritus model (KELLER ET AL., 2012). The 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 at the sea surface to 500 m in the deep ocean. We use a sub-grid scale bathymetry as described in SOMES ET AL. (2013) to simulate benthic fluxes of phosphorus. The sub-grid bathymetry is inferred from the ETOPO2v2* and represents global spatial distributions of continental shelves, slopes and other topographical features (1/5°). For the topography used here, the shelf (0-200 m) covers 6.5%, the slope (200-2000 m) 11.7% and the deep sea (>2000 m) 81.9% of the global ocean. Downward fluxes of organic matter are intercepted by the sub-grid bathymetry related to the fractional sediment cover for each ocean grid box, and benthic fluxes of phosphorus are calculated based on the transfer functions described in the following section.

2.2 Phosphorus Cycle in UVic Model

Earlier applications of the UVic ESCM assumed a fixed marine P inventory. We included a representation of the dynamic P cycle for this study. It consists of a modified terrestrial weathering module (MEISSNER ET AL., 2012) and a redox-sensitive transfer-function for burial and benthic release of P (FLOEGEL ET AL., 2011; WALLMANN, 2010).

The continental-weathering module developed earlier for fluxes of dissolved inorganic carbon (DIC) and alkalinity (MEISSNER ET AL., 2012; LENTON & BRITTON, 2006), is based on the following equations:

$$F_{DIC,w} = F_{DIC,w,0} * \left[f_{Si} + f_{Ca} * \left(\frac{NPP}{NPP_0} \right) * \left(1 + 0.087 * (SAT - SAT_0) \right) \right] = F_{DIC,w,0} * f(NPP,SAT)$$
 (1)

 $F_{Alk,w} = F_{Alk,w,0} * \left(\frac{NPP}{NPP_0}\right) * \left[f_{Si} * (1 + 0.038) * (SAT - SAT_0) * 0.65^{0.09} * (SAT - SAT_0)\right] + f_{Ca} * (1 + 0.087 * (SAT - SAT_0)) (2)$

^{*} https://www.ngdc.noaa.gov/mgg/global/etopo2.html

Where $F_{DIC,w}$ and $F_{Alk,w}$ represent the globally integrated flux of DIC and alkalinity via river runoff, f_{Si} and f_{Ca} stand for the fraction of silicate (0.25) and carbonate (0.75) weathering, and NPP and SAT are the global mean net primary production on land and global mean surface air temperature over land (in degrees Celsius). The index 0 stands for preindustrial values.

We added the following flux to account for P weathering $(F_{DP,w})$ with the same dependencies on globally and annually averaged net primary production (NPP) and surface air temperature (SAT) as those for DIC:

$$F_{DP,w} = F_{DP,0} * f (NPP, SAT)$$
(3)

The global river input of dissolved inorganic P (DIP) is the only continental source for P in the model. The global DIP input is distributed over all coastal points of discharge scaled according to their individual volume discharge. The pre-industrial DIP input to the ocean (F_{DP,0}) is assumed to be in steady state and in equilibrium with the total globally integrated preindustrial net burial of P (BUR_P):

$$F_{DP,0} = BUR_{P,0} \tag{4}$$

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We use an empirical transfer function for BUR_P and for the benthic release of DIP (BEN_{DIP}) derived from observations across bottom-water oxygen gradients (WALLMANN, 2010; FLÖGEL ET AL., 2011). The release of dissolved inorganic P (BEN_{DIP}) is calculated as follows:

$$20 \quad BEN_{DIP} = \frac{BEN_{DIC}}{r_{reg}} \tag{5}$$

Benthic release of dissolved inorganic carbon (BEN_{DIC}) is calculated from an empirical transfer function (Fig. 2 in FLÖGEL ET AL., 2011) to determine BEN_{DIP} fluxes at the ocean bottom. In our model configuration POC is remineralised completely at the ocean bottom and no ocean-to-sediment-fluxes of POC occur, i.e. BEN_{DIC} = RR_{POC}, where RR_{POC} denotes the rain rate of particulate organic carbon to the sediment. WALLMANN (2010) calculated r_{reg} by a regression of observational data to bottom-water oxygen concentrations:

$$r_{reg} = \frac{RR_{POC}}{BEN_{DIP}} = Y_F + A * \exp\left(\frac{-[O_2]}{r}\right)$$
 (6)

The regeneration ratio is calculated by dividing the depth-integrated rate of organic matter degradation in surface sediments (RR_{POC}) by the benthic flux of dissolved inorganic P into the bottom water (BEN_{DIP}). Parameters are defined as $Y_F = 123 \pm 123$

24, A = -112 \pm 24 and r = 32 \pm 19 and O_2 is in μ mol/l (WALLMANN, 2010). Under oxic conditions r_{reg} is higher than the Redfield ratio (106; REDFIELD ET AL., 1963) and under oxygen-depleted conditions r_{reg} reduces to 10 (WALLMANN, 2010).

The rain rate of POP (RR_{POP}) is calculated by the rain rate of POC (RR_{POC}) divided by the Redfield <u>ratio</u>. As a result BUR_P can be calculated as follows:

$$BUR_P = RR_{POP} - BEN_{DIP} (7)$$

The burial of P (BUR_P) in the sediment is equal to the rain rate of particulate organic P (RR_{POP}) minus BEN_{DIP} (FLOEGEL ET AL., 2011). If the benthic release overcomes the rain rate of POP at depths below 1000 m, the burial is set to zero. Following FLOEGEL ET AL. (2011), this condition is not applied to shallower sediments because these deposits receive both marine particles and high fluxes of riverine particulate phosphorus.

2.3 Model Simulations

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Two model simulations were performed. Our control simulation, called simulation REF hereafter, includes <u>neither</u> weathering, benthic <u>release</u>, <u>nor burial</u> of P. The global amount of P in the ocean is therefore conserved in this simulation over time. The second simulation, called WB, includes P weathering <u>as well as</u> benthic <u>burial and release</u> of P <u>but excludes</u> <u>additional anthropogenic input.</u> The spin up <u>was</u> performed by computing the <u>burial and</u> benthic <u>release</u> according to Eq. 6. The weathering fluxes were set to a value to compensate the burial rate (Eq. 4) during the spin up but not thereafter.

After a spin-up of 20,000 years under preindustrial boundary conditions, we forced the model with anthropogenic CO₂ concentrations following the RCP 8.5 scenario of the IPCC AR5 assessment (MEINSHAUSEN ET AL., 2011; RIAHI ET AL., 2011). The CO₂ emissions in the UVic ESCM reach 105.6 Pg CO₂ a⁻¹ in year 2100. Between years 2100 and 2150 the models are forced with constant CO₂ emissions (105 Pg CO₂ a⁻¹), followed by a linear decline until year 2250 to a level of 11.5 Pg CO₂ a⁻¹ and then linearly to zero emissions in year 3005 (see Fig. 2a). Simulated atmospheric CO₂ concentrations peak in year 2250 with 2148.6 ppmv and equal 1835.8 ppmv in year 3005 (see Fig. 2a).

25 2.4 Simulated preindustrial equilibrium

The UVic ESCM has been validated under present day and preindustrial conditions in numerous studies (EBY ET AL., 2009; WEAVER ET AL., 2001). In particular, KELLER ET AL. (2012) recently compared results of its ocean biogeochemical component to observations and previous model formulations. We therefore concentrate our validation on the new model component in this study, the P cycle.

Estimates of <u>preindustrial</u> burial rates vary over a wide range in the literature. <u>The comprehensive review by SLOMP</u> (2011) reported a burial rate of 0.032-0.35 Tmol P a⁻¹ for the total ocean while BATURIN (2007) suggests a burial rate of 0.419 Tmol

P a⁻¹ based on <u>observational</u> data described in detail by WALLMANN (2010). The burial rate diagnosed by the UVic ESCM <u>in simulation WB for the total ocean under preindustrial boundary conditions</u> (0.38 Tmol P a⁻¹), is within range of these earlier estimates. The burial at the continental margin (0-200 m) accounts for 50-84% of total burial corresponding to 0.016-0.175 Tmol P a⁻¹ calculated in SLOMP (2011). RUTTENBERG (2004) estimated a burial rate at continental margins of 0.15-0.22 Tmol P a⁻¹, while the UVic ESCM calculated a burial rate of 0.33 Tmol P a⁻¹ for the continental margins in year 1775. The open ocean burial contributes only a minor part to total burial (0.04-0.13 Tmol P a⁻¹; RUTTENBERG, 2004; in the UVic it is 0.046 Tmol P a⁻¹).

To conserve marine P during long model spin ups, the dissolved weathering flux of P under preindustrial conditions is set equal to the diagnosed total burial rate during the spin-up, 0.38 Tmol P a⁻¹. Following the method of calculating the reactive P flux (defined in RUTTENBERG (2004) as the sum of >50% of TDP (=DOP) plus 25-40% of particulate P flux), our result fits well with estimates summarised by SLOMP (2011) ranging from 0.13 Tmol P a⁻¹ (natural P flux) to 0.36 Tmol P a⁻¹ (modern P flux) and RUTTENBERG (2004) (0.16-0.32 Tmol P a⁻¹).

Global values for benthic release under preindustrial conditions equal 0.78 Tmol P a⁻¹ in the UVic ESCM (simulation WB)_a while RUTTENBERG (2004) described a range from 0.51 Tmol P a⁻¹ to 0.84 Tmol P a⁻¹ based on pore water measurements (COLMANN & HOLLAND, 2000) for coastal regions. For the deep sea COLMANN & HOLLAND (2000) specified the benthic release value with 0.41 Tmol P a⁻¹. In the UVic ESCM the benthic release for continental margins was calculated as 0.4816 Tmol P a⁻¹ and for the open ocean as 0.2951 Tmol P a⁻¹.

3 Results

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3.1 Simulated Climate

The global mean atmospheric surface temperature, as simulated by the WB run, increases until year 2835 and peaks at 23.1°C, i.e. 9.9°C above pre-industrial levels. Simulation REF shows similar changes in temperature with an increase until year 2855 and a peak at 23.3°C (see Fig. 2a). Both simulations show a slight recovery in temperatures after the peak (REF: 23.2°C; WB: 23.1°C; year 3005). Atmospheric temperatures in the WB-simulation are slightly lower than in the reference simulation, due to slightly lower carbon dioxide concentrations in the atmosphere, caused by increased global ocean alkalinity (REF: 2.498 mol m⁻³; WB: 2.481 mol m⁻³; both for year 3005), the enhanced biological pump and a rise in detritus export rate (see Sect. 3.2), and therefore increased marine uptake of atmospheric CO₂. The impact of the negative feedback via enhanced biotically and chemically induced marine uptake of atmospheric CO₂ on surface air temperatures is thus small compared to the CO₂ induced warming in a high-emission scenario.

Given that the response in temperature is similar for both simulations <u>compared to considerable differences in biological</u> <u>productivity (see below)</u>, differences in oxygen concentration mainly originate from biogeochemical changes, which will be discussed <u>in Sect. 3.3</u>.

3.2 Phosphorus Dynamics

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The weathering rate (see Fig. 3b) and associated flux of P into the ocean via river discharge more than doubles relative to the pre-industrial situation in our WB-simulation and leads to an enhancement in global mean oceanic P concentrations by 27% over 1000 years (see Fig. 2b). At the same time, benthic burial acts as the only P sink in our model (see Figure S1), mitigating the total increase in marine P. The P concentration remains constant in the control run REF.

The weathering input in the WB-simulation is largest north of 30°N (0.338 Tmol P a⁻¹ in year 3005; see Fig. 3a), while south of 30°S (0.138 Tmol P a⁻¹) and in the low latitude Pacific Ocean the input is lowest (0.117 Tmol P a⁻¹). Weathering fluxes into the low latitude Indian and Atlantic Oceans equal 0.187 and 0.267 Tmol P a⁻¹, respectively.

Increasing P concentrations as well as climate warming result in an increase in net primary production in the ocean (ONPP). Globally integrated ONPP ranges between 43.8 Tmol P a⁻¹ (REF) and 44.1 Tmol P a⁻¹ (WB) under preindustrial conditions and 65 Tmol P a⁻¹ (REF) and 116.4 Tmol P a⁻¹ (WB) at year 3005 (see Figure S1). The main areas of ONPP increase are located in the tropical ocean, where higher temperatures favour net primary production in the model (results not shown).

Due to enhanced P inventory and enhanced ONPP, the WB-simulation also has a higher export rate (8.6 Tmol P a⁻¹, computed at 130m depth; see Fig. 2b) when compared to the reference run (5.5 Tmol P a⁻¹) in year 3005. In the REF simulation, the export rate declines until year 2175 (4.8 Tmol P a⁻¹) in response to enhanced stratification, associated declining nutrient supply and stronger nutrient recycling in the upper layers (SCHMITTNER ET AL., 2008; STEINACHER ET AL., 2010; BOPP ET AL., 2013; MOORE ET AL., 2013; YOOL ET AL., 2013; KVALE ET AL., 2015). The export rate recovers to reach 5.5 Tmol P a⁻¹ at the end of the simulation in experiment REF.

The globally integrated remineralisation rate <u>in the aphotic zone</u> (results not shown) ranges between 5.1 Tmol P a⁻¹ (WB) and 5.2 Tmol P a⁻¹ (REF) in year 1775. Simulation WB is characterized by a strong increase in remineralisation until 3005 with a maximum of 8.1 Tmol P a⁻¹ (in year 3005), while in the reference run the remineralisation rate first decreases, followed by a moderate increase to 5.3 Tmol P a⁻¹. Regions with highest remineralisation are located on the continental margins, especially in the Indian Ocean.

The P burial in the WB-simulation equals 0.38 Tmol P a⁻¹ in year 1775 and decreases by 44.3% to 0.2 Tmol P a⁻¹ in year 3005 (see Figure S1). One reason for this decrease is the redox-state of the bottom water. The strong expansion of the area of ocean bottom waters with O₂ concentrations below 0.005 mol m⁻³ (see Fig. 2d) in the WB simulation leads to a decrease in benthic burial of P despite an increase in the rain rate of particulate organic P, RR_{POP}. In general, burial rates are largest along the coastal margins, where 87.9% of the total flux is buried in 1775. Highest increases in burial rates between years 1775 and 3005 are located in the Arctic Ocean (see Fig. 4a), whereas burial rates decrease in the Bay of Bengal and the Gulf of Mexico where low-oxygen bottom waters expand (see Fig. 5).

The benthic P release in the WB simulation increases by 119% until year 3005 to 1.7 Tmol P a⁻¹ (see Figure S1). As mentioned above, the benthic release is a redox-dependent process, which commonly takes place at the coastal margins (WALLMANN, 2010; in our model under preindustrial conditions 62% of total release is from coastal margins). This means

that an increase in suboxic bottom water area (see Fig. 2d) leads to an enhanced release of benthic P in WB. A rapid increase between years 1775 and 3005 can be found in the Bay of Bengal, the Gulf of Mexico and in the Arctic Ocean (see Fig. 4b). In our model simulations, both the weathering-induced P flux into the ocean (see Fig. 2c) as well as the net P released from the sediments (see Fig. 2c) show a strong increase under continued global warming, which explains the increase in the marine P inventory in the WB simulation (see Fig. 2b). However, the simulated increase in the weathering input has a much stronger (about 4 times larger) impact on the P budget and therefore on the expansion of OMZs than the benthic release feedback (see Fig. 2c). We note that even at the end of the thousand-year simulation, the P cycle has not yet reached a new steady state in experiment WB. Weathering rates are high in the warm climate and burial of P has not increased to counteract the supply by weathering (see Fig. 3b & S1). The release of P from sediments also adds to this imbalance. As a result, the marine P inventory is still increasing almost linearly at the end of our simulation. Extending the simulation until year 10,000 reveals that the ocean - as well as the coastal regions - do not become anoxic despite a more than 3-fold increase in oceanic P inventory (see Sect. 3.3 & Supplement Figure S 2) while the P cycle still exhibits a strong imbalance between sources and sinks.

3.3 Oxygen Response

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The black contours in Fig. 5 indicate the lateral extent of OMZs for a depth of 300 m (see Figure S3 for a depth of 900 m). In year 1775, the suboxic volume, defined here as waters with oxygen concentrations of less than 5 mmol m⁻³, equals 3.9x10⁶ km³ in both simulations (see Fig. 2d). An observational estimate of today's suboxic water volume equals 102x10⁶ ± 15x10⁶ km³ for oxygen concentrations less than 20 mmol m⁻³ (PAULMIER & RUIZ-PINO, 2009), which is considerably larger than the volume of O₂<20 mmol m⁻³ waters in our WB-simulation (WB₂₀₀₅ = 15.8x10⁶ km³). However, in consideration of the studies of BIANCHI ET AL. (2012) and their calculated OMZ volume of 2.28-2.78*10⁶ km³, as well as World Ocean Atlas (WOA₂₀₀₅ = 4.12*10⁵ km³), it can be concluded that estimations of the volume of OMZs vary over a wide range and that our results are within this range. Comparing our results with observational data from the WOA₂ a generally good agreement can be found with regard to the spatial distribution of low-oxygen waters (see Fig. 5). The suboxic areas are located in the upwelling regions of the tropical eastern Pacific and eastern Atlantic as well as in the Indian Ocean (see Fig. 5; representative for both simulations in 1775).

During our transient simulations, we find a considerable expansion of OMZs until year 3005 in both simulations (see Fig. 2d and Fig. 5). The expansion of the suboxic volume between 300 and 900 m is particularly pronounced in the WB simulation where the OMZs account for 4.85×10^7 km³ in year 3005, i.e. an increase by a factor 12.4. The control simulation (REF) shows a much smaller increase in the volume of OMZs (1.12×10^7 km³ between 300 and 900 m depth). As both simulations display similar climates (see Fig. 2a), the difference in the oxygen fields is largely due to the differences in the simulated P cycle.

The sea-floor area in contact with suboxic bottom waters, which directly impacts the redox-sensitive benthic burial and P release, shows an increase by more than a factor of 19 (WB₁₇₇₅= 3.59×10^5 km²; WB₃₀₀₅= 6.95×10^6 km²) in the WB simulation

(see Fig. 2d) compared to a factor of 4 increase in the REF simulation (REF₁₇₇₅= $2.79 \times 10^5 \text{ km}^2$; REF₃₀₀₅= $1.2 \times 10^6 \text{ km}^2$). Our present-day results (WB₂₀₀₅ = $3.8 \times 10^5 \text{ km}^2$) compare well with data of the WOA (WOA₂₀₀₅ = $2.48 \times 10^5 \text{ km}^2$).

Somewhat unexpectedly, in our study an increase in continental weathering does not result in an anoxic ocean under current topography and seawater chemistry - at least not until year 10,000. At the preindustrial state (year 1775), 0.12% of all coastal margins are characterized by oxygen concentrations below 0.005 mol m⁻³. While this portion increases by about a factor of 50 to 5.57% by year 3005, this is too low for the generation of widespread coastal anoxia. Conversely, the global mean oxygen concentration starts to increase again in year 3415 when it has reached a minimum of about two thirds of the preindustrial oxygen inventory in the WB simulation (see Figure S1). This suggests that the positive feedback between the release of benthic P and marine net primary production is - in this study for present day bathymetry and geography - not the decisive factor for a rapid transition into an anoxic ocean.

4 Uncertainties

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Although the model's subcomponents for weathering, burial and benthic release rates are highly simplified in this study, the simulated global P fluxes fall within the range suggested by earlier studies and observational estimates (PALASTANGA ET AL., 2011; FILIPPELLI, 2002; BATURIN, 2007; WALLMANN, 2010). The weathering fluxes are calibrated against global mean burial rates under an implicit steady-state assumption, although it is unclear whether the pre-industrial P cycle in the ocean was in equilibrium (WALLMANN, 2010). The relatively high P weathering fluxes as well as the assumed indefinite P reservoir in the shelf sediments in our simulations might lead to an overestimation of the effects on the P cycle and OMZs.

In our model, the increase in the P inventory results in a strong increase in ONPP. Contrary to other studies, e.g. GREGG ET AL. (2005) or BOYCE ET AL. (2010), in our study the temperature effect overcompensates the stratification effect as described by SARMIENTO ET AL. (2004), TAUCHER & OSCHLIES (2011) and KVALE ET AL. (2015) and thus leads to an increase in ONPP also in the reference run. While the net effect of warming on ONPP is not well constrained and differs considerably among models, the impact of changing environmental conditions on export production appears to be better constrained (TAUCHER & OSCHLIES, 2011). In agreement with simulations by other models, experiment REF shows a stratification-induced decline in export production, while the increase in P induces an increase in export production in WB. Although we use a coarse resolution model, the applied sub-grid scale bathymetry allows the calculation of more accurate benthic burial and release fluxes than otherwise possible with such a model.

It should also be noted that the benthic release feedback on OMZs might have been more efficient <u>under Cretaceous</u> <u>boundary conditions</u> because the shelf area was considerably larger due to higher sea levels (late Cretaceous shelf area: $46x10^6 \text{ km}^2$; present day shelf area: $26x10^6 \text{ km}^2$ (BJERRUM ET AL., 2006)). <u>Cretaceous topography</u> might <u>therefore have induced a stronger</u> benthic release feedback <u>as</u> shown in TSANDEV <u>& SLOMP</u> (2009).

FILIPPELLI (2002) showed in his study that due to the anthropogenic activities the global, total present-day river input of P has doubled in the last 150 years. In our study the direct anthropogenic influence, such as agricultural input of P into the

system, <u>is</u> excluded and should be considered in future studies even though the human impact is projected to decrease until year 3500 (FILIPPELLI, 2008). FILIPPELLI (2008) <u>and HARRISON ET AL. (2005)</u> estimated a rate of 0.03 Tmol P a⁻¹ <u>and 0.7 Tg P a⁻¹ (=0.023 Tmol P a⁻¹), respectively, for anthropogenic P delivered to the ocean <u>as a result of</u> fertilization, deforestation and soil loss as well as sewage in year 3000. In comparison to <u>our simulated maximum weathering value</u> of 1.09 Tmol P a⁻¹ until year 3005, the <u>direct anthropogenic impact seems to be small.</u></u>

5 Conclusions

This study constitutes a first approach to estimate the potential impact of changes in the marine P cycle on the expansion of global ocean OMZs under global warming on millennial time scales. Model simulations show that the warming-induced increase in terrestrial weathering (see Fig. 3b) leads to an increase in marine P inventory (see Fig. 2b) resulting in an intensification of the biological pump, corroborating the findings by TSANDEV & SLOMP (2009). As a consequence, oxygen consumption as well as the volume of OMZs increase in our simulations by a factor of 12 over the next millennium (see Fig 2d and 5).

The positive feedback involving redox-sensitive benthic P fluxes - where the expansion of OMZs leads to an increase in benthic release of P (see Fig. 2c & Fig. S1), which in turn enhances biological production and subsequent oxygen consumption (WALLMANN 2010) - has only limited relevance for the expansion of OMZs in this study. Instead, a negative feedback dominates that involves enhanced weathering and P supply to the ocean, an intensification of the biological carbon pump and associated marine uptake of atmospheric CO₂. The atmospheric CO₂ impacts the surface air temperature through a negative feedback loop, which limits the warming and weathering and, eventually, the expansion of the OMZs. We can therefore conclude that, based on the parameterizations used in this study, the P weathering and biological pump feedback outcompetes the redox-sensitive benthic P-release feedback on millennial timescales. Although the ocean does not become anoxic in our simulations, the benthic P-release feedback may have played a role in past oceanic anoxic events. An increase in shelf areas due to higher sea levels, such as during the Cretaceous, would have led to a more powerful benthic P-release feedback as a much larger sediment area could have been in contact with low-oxygen bottom waters. Whether this different bathymetry alone could result in a more dominant benthic P-release feedback needs to be investigated in future studies.

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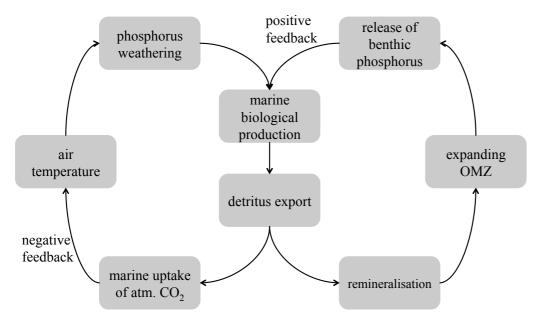


Figure 1: Possible feedbacks in the global phosphorus cycle under climate warming conditions.

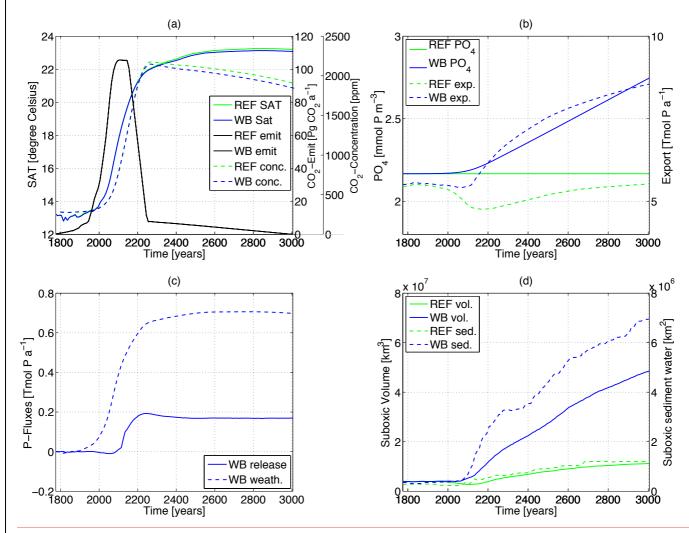


Figure 2: Global and annual mean time series of (a) surface air temperature in degree Celsius (solid lines), CO_2 -emissions in Pg CO_2 a⁻¹ (black solid line (for both simulations)) and CO_2 -concentration in ppm (dashed lines); (b) global mean phosphorus concentration in mmol P m⁻³ (solid lines) and export rate in Tmol P a⁻¹ at 130 m depth (dashed lines); (c) anomalies of phosphorus input via sediment in Tmol P a⁻¹ (solid line) and anomalies of phosphorus weathering input in Tmol P a⁻¹ (dashed line); (d) suboxic volume (<0.005 mol m⁻³) of the ocean in km³ (solid lines) and surface of ocean bottom layer with O_2 concentrations below 0.005 mol m⁻³ in km² (dashed lines). The control simulation (REF) is shown in green, simulation WB in blue.

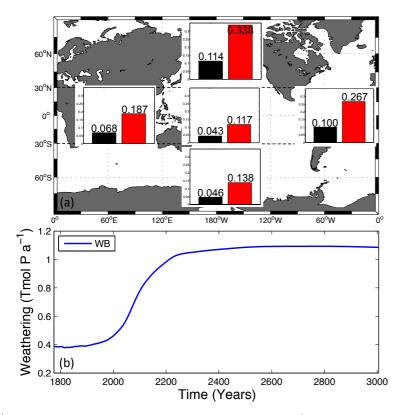


Figure 3: (a) Phosphorus weathering input (in Tmol a⁻¹) into the <u>tropical</u> Pacific Ocean (middle), <u>tropical</u> Atlantic Ocean (right, middle), <u>tropical</u> Indian Ocean (left, middle), Northern Oceans (=oceans north of 30° N; upper middle) and Southern Ocean (=ocean south of 30° S; lower middle) in 1775 (black bars) and 3005 (red bars). (b): Annual mean averaged phosphorus weathering input (global sum) of 1775 until year 3005.

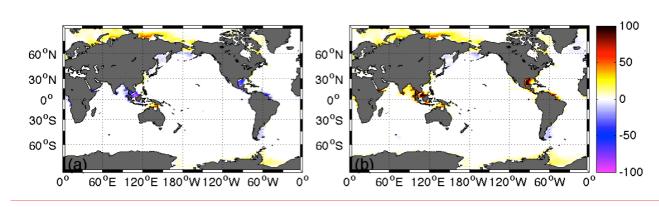


Figure 4: Difference (year 3005 minus year 1775) in (a) burial and (b) benthic release flux in mmol P m⁻² a⁻¹ for simulation WB.

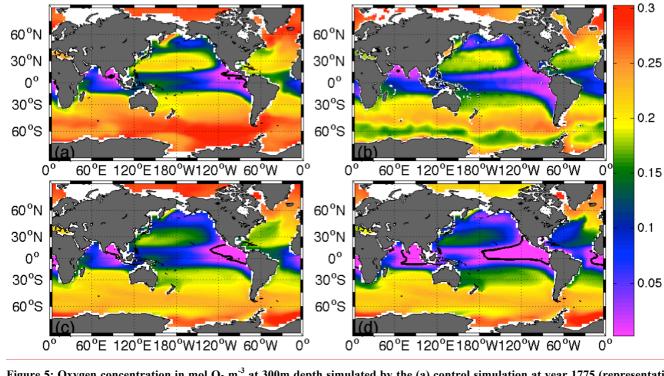


Figure 5: Oxygen concentration in mol O_2 m⁻³ at 300m depth simulated by the (a) control simulation at year 1775 (representative for both REF and WB model runs in year 1775), (b) the World Ocean Atlas in 2009, (c) the control simulation at year 3005 and (d) simulation WB at year 3005. The black contour lines at 0.005 mol m⁻³ highlight the oxygen minimum zones (OMZs).