

Author's response

“BPOP-v1 model: exploring the impact of changes in the biological pump on the shelf sea and ocean nutrient and redox state”

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Dear Editor,

Thank you for your answer. We have gone through a new round of revisions and address below your new questions and comments. We apologize for having forgotten to address the specific comments of Referee nr.2. We are including our answers below. We have also uploaded these answers in a separate file as an Author's comment in the public discussion page.

We include our new answers below in the following order:

- 1) Revisions round 2: comments and answers;
- 2) Revisions round 1: answers to previous comments, updated according to the new changes in the model;
- 3) revised manuscript with track changes.

We look forward to your response.

Sincerely,

Elisa Lovecchio

Revisions Round 2

Answer to Editor's Comments

We thank the Editor for his comments and suggestions, which we copy below (in blue), and explain in detail our related changes to the manuscript (in red) and model.

EC1) Table 5: is there a reason why "deep ocean" is mentioned in the "total ocean O₂" row?; is it not more straightforward to just use total ocean O₂?

We are now using the total ocean O₂ reservoir estimates.

EC2) Table 5: regarding "production (prod)", I think that the upper span of the range here may have been miscalculated; the Carr et al. (2006) reference confusingly refers to estimates based on 6 months of data, but the units used suggest a maximum PP of ~60 Pg C / y (5000 Tmol C / y in your units); Figure 5a of the paper has a single GCM with a PP close to ~80 Pg C / y (6667 Tmol C / y in your units); also, why are you using Tmol C / y when Pg C / y is the more common unit, and its non-SI equivalent, Gt C / y is used in Carr et al., 2006?

Thank you very much for this correction, we have updated Table 5 and changed the production units accordingly. The full Table 5 can be found in the updated answer to the Editor's comments from round 1 (below).

EC3) Figure 3b: you could dispense with this blow-up by plotting both a and c here on a log(time) scale; this would expand the most interesting period of the model's evolution; however, you may have already tried this and decided against it

Thank you for your suggestion, we have tried to use a log(time) scale, but prefer to maintain the current plotting style for Figure 3.

*EC4) Figure 3b caption: "in the *first* two hundred thousand years"*

Thank you.

EC5) Page 6 of your response: you say "Anaerobic remineralization releases its product to the atmosphere" but this is unclear to me; releases its product to the atmosphere?; this is the sediments we're talking about, no?; one would assume they were quite isolated from the atmosphere

In our model, the reducing agent produced by anaerobic remineralisation is methane gas and it is only produced when the sediments and the deep shelf water column have gone anoxic. As we do not track other oxidising agents such as SO₄ there is nothing for the methane to be oxidised by until it reaches the surface ocean, and as the surface ocean is equilibrated with the atmosphere, the fact that we assume oxidation in the atmosphere is a reasonable approximation. A more elaborate

model would recognise other oxidants, notably SO_4 , and this would transfer some of the oxygen consumption to deep waters, tending to make them more anoxic. Hence our results can be seen as minimum estimates of deep shelf anoxia. (Anaerobic sediment remineralization only matters in the deep shelf, as the deep ocean doesn't really accumulate any organic matter in the sediments and never reaches suboxic levels.)

We have further explained this in our manuscript by adding the following sentences to subparagraph 2.2.5:

In our model, the reducing agent produced by anaerobic remineralisation is methane gas and it is only produced when the sediments and the deep shelf water column have gone anoxic. As we do not track other oxidising agents such as SO_4 there is nothing for the methane to be oxidised by until it reaches the surface ocean, and as the surface ocean is equilibrated with the atmosphere, the fact that we assume oxidation in the atmosphere is a reasonable approximation.

EC6) Page 7 of your response: has any of this made it into the manuscript or its supplementary material; this would be a reasonable addition to the latter if it's not already there; and it's would be of interest / value to readers in any case

We have decided to refer to this sensitivity experiment in subsection 5.1.3 of the Discussion section of the paper, adding the following sentences:

Furthermore, we have tested the impact of having sediment remineralization rates that vary with the particles' z_{rem} , under the assumption that the liability of small and large particles may be different. In our experiment, we increased the remineralization rm_r rate linearly with z_{rem} by 40 % of our baseline value (rm_r^0), with rm_r^0 being found at the centre of the interval of explored values of $z_{\text{rem}} = [0 \text{ m}, 450 \text{ m}]$. Under these conditions, we obtained a higher decoupling between the influence of z_{rem}^S and z_{rem}^L on budgets and fluxes, both being more strongly driven by the small particle properties for large values of z_{rem}^L .

EC7) Table 3 in the revised manuscript: this O2:P ratio was mentioned by referee 2 but the point was not addressed in the authors' response, and does not appear to have been changed either

EC8) More generally, it's not completely clear whether you have addressed the specific comments from referee 2; the preceding point would rather suggest not

Unfortunately, while revising the manuscript and preparing our answers we have forgotten to address the specific comments of Referee nr.2. We have now answered them and included our changes to the model below. Due to this latter changed we have further retuned the model around modern ocean values. We refer to the answer to EC2 of the revision round one for a more detailed discussion of the applied changes to the model.

Answer to Anonymous Referee nr.2

We thank Anonymous Referee nr.2 for their specific comments, and apologize for having forgotten to address them in our initial answer. We include our answers below, highlighting the Referee's comments in blue and our changes to the manuscript in red.

SC 1) Key paper not cited: Reinhard CT., Planavsky NJ et al. "Evolution of the global phosphorus cycle." Nature 541, no. 7637 (2017): 386.

Thank you for your suggestion, we have added the reference in the manuscript's discussion.

SC 2) Equations 14 & 17: AirSea should appear the same in both

Thank you, we have corrected it.

SC3) Equation 17: why does anaerobic remineralisation remove oxygen?

In our model, the reducing agent produced by anaerobic remineralisation is methane gas and it is only produced when the sediments and the deep shelf water column have gone anoxic. As we do not track other oxidising agents such as SO_4 there is nothing for the methane to be oxidised by until it reaches the surface ocean, and as the surface ocean is equilibrated with the atmosphere, the fact that we assume oxidation in the atmosphere is a reasonable approximation.

We have added this discussion to our manuscript in subparagraph 2.2.5 in order to clarify our equations.

SC 4) Line 5 of page 7: anaerobic remineralisation of organic matter also releases phosphorus (in fact oxygen-depleted sediments are stronger sources of phosphorus to the overlying water column).

We agree with Referee nr.2 and we have modified our model accordingly, following the suggestions of one of the major comments of Referee nr.1. We refer to our answer to the comment R1C1 (Referee nr.1, comment nr.1) for a detailed description of the changes to the model.

SC 5) Table 1: moles of air or moles of oxygen in the atmospheric box?

Oxygen in the atmospheric box is expressed in terms of its mixing ratio [mol mol^{-1}]. We have added a table (Table 1) with the list of the variables and of their units.

SC 6) Table 2: the Redfield ratio of oxygen to phosphorus ($-\text{O}_2:\text{P}$) is $\sim 150:1$ not $106:1$ (see for instance: Anderson, L.A. and Sarmiento, J.L., 1994. Redfield ratios of remineralization determined by nutrient data analysis. Global biogeochemical cycles, 8(1), pp.65-80; Thomas, H., 2002. Remineralization ratios of carbon, nutrients, and oxygen in the North Atlantic Ocean: A field databased assessment. Global biogeochemical cycles, 16(3)).

We thank Referee nr.2 for their comment. Our latest version of the model adopts the suggested value O₂:P=150:1, and we have updated this value in Table 3.

SC 7) W₀ is a baseline flux (line 3 of page 4), hence cannot have units of mmol if equation 3 is to be dimensionally plausible.

Thank you, we have corrected it. The correct unit is: mmol yr⁻¹ (see Table 3).

Revisions Round 1 (updated)

Answer to Editor's Comments

We thank the Editor for his comments and suggestions, which we copy below (in blue), and explain in detail our related changes to the manuscript (in red) and model.

EC 1) Evaluation of your model (page 7) might benefit from a table which compares each of the quantities to the corresponding observational estimate (e.g. see Table 2 of Yool & Tyrrell, GBC, 2002)

In agreement with this suggestion, we have added an evaluation table (**Table 5** of the revised manuscript) with the updated results of our model evaluation after revisions. We have updated our comments on the model evaluation in the related section 3.2 of the manuscript.

The table reads as follows:

Quantity	Model	Modern values or estimates	Units	Source
Total ocean P	2500 - 2800	3100	TmolP	Watson et al. (2017)
Total ocean O₂	100 - 140	225-310	PmolO ₂	Duursma and Boisson (1994);Keeling et al. (1993)
P^{ss}	1.5 – 1.9	1 – 1.5	mmol m ⁻³	Garcia et al. (2018b);Sarmiento and Gruber (2006)
P^{ds}	3.9 – 5.4	2.2	mmol m ⁻³	Garcia et al. (2018b);Watson et al. (2017)
P^{so}	0.4 – 1.1	0.2 - 2	mmol m ⁻³	Garcia et al. (2018b);Sarmiento and Gruber (2006)
P^{do}	2.0 – 2.3	1 - 3	mmol m ⁻³	Garcia et al. (2018b);Sarmiento and Gruber (2006)
O^{ss}	273 - 274	200 - 350	mmol m ⁻³	Garcia et al. (2018a)
O^{ds}	2.8 – 12.3	0 - 80	mmol m ⁻³	Garcia et al. (2018a)
O^{so}	273	200 - 350	mmol m ⁻³	Garcia et al. (2018a)
O^{do}	72 - 110	40 - 200	mmol m ⁻³	Garcia et al. (2018a)
Production (Prod)	18.8 – 51.5	35 - 80	GtC yr ⁻¹	Carr et al. (2006)
Export	2.8 – 4.0	4 – 20	GtC yr ⁻¹	Henson et al. (2011)
Export production	8 % - 30 %	2 % - 20 %	of total Prod	Boyd and Trull (2007)
Burial	0.3 % - 0.8 %	0.4 %	of total Prod	Sarmiento and Gruber (2006)
Shelf sea production	12 % - 25 %	20 %	of total Prod	Barrón and Duarte (2015);Wollast (1998)
Shelf sea export	21 % - 27 %	29 %	of total Export	Sarmiento and Gruber (2006)
Shelf sea burial	100 %	91 %	of total Burial	Sarmiento and Gruber (2006)

Table 5: Summary of the model evaluation provided in section 3. Modern observations and estimates are compared to model results obtained for z_{rem}^L in the range of measured values for a modern shelf sea (Cavan et al., 2017).

EC 2) I'm a little surprised that you haven't tuned your productivity to more realistic values, and that you lay the blame for your model's low productivity on its implicit microbial loop and missing distinction of new / regenerated production; it should be possible to achieve more realistic levels of productivity through tuning, and other models (again, Yool & Tyrrell, 2002) have no such difficulties while having the same limitations

Following the modifications to the model's equations in agreement with the suggestions of Referee nr.1 and Referee nr.2, we have further retuned the model towards more realistic values of production and export. This was done by slightly modifying a few biogeochemical parameters (coagulation rate, remineralization rate, Ca-P formation rate) and mixing in the shelf. Further changes to the model, following recent literature, consisted in distinguishing between a water column and a sediment half saturation constant for aerobic remineralization. The combination of these changes in the equations and in a few parameter values allowed us to increase production and export (bringing them closer to the lower end of modern estimates), while still maintaining the values of export production and burial to export ratio in the range of current estimates. We modified the discussion of the model evaluation (subsection 3.2) accordingly.

EC 3&4) Although you mention the timescales over which you model can easily be run (as well as alluding to simulating it across the Phanerozoic), none of your figures show the time evolution of your model; it might be informative for readers were you to include some indication of the model's time-evolution from, say, the arbitrary initial conditions that you list in Table 2 (e.g. see Figure 5 of Yool & Tyrrell, 2002)

On a related point, how does your model compare in terms of residence times of the elements it represents?; given that it includes river inputs of P and reasonably represents ocean concentrations, I would expect it to do a good job here, but it might still be worth drawing attention to this

To address this comment, we have included in the manuscript an additional figure (revised paper's **Figure 3**) to show an example of modelled tracer evolution. Furthermore, we have divided the Evaluation section in two parts with an initial subsection 3.1 focusing on the model dynamics and a second subsection 3.2 focusing on the comparison to model ocean budgets and fluxes (which corresponds to the old Evaluation before revisions).

Subsection 3.1 of the revised manuscript reads as follows:

3.1 Timescales

Starting from the initial values listed in Table 3, the modelled state variables evolve towards equilibrium for any couple of values of $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ in the explored interval. Simple mass conservation checks show no hidden source or sink of tracers in the model's boxes. Figure 3 illustrates an example of evolution of the variables for $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ in the middle of the interval of explored values for both particle types. In all the ocean boxes, P shows an initial oscillation that evolves on timescales of tens of thousands of years (Figure 3a,b), as expected by the typical timescale of evolution of the tracer (Lenton and Watson, 2000). This is followed by a slower drift which depends on the dynamics of the deep water oxygen content, as the release and burial of P in the sediments depends on the level of oxygenation of the deep ocean and especially of the deep shelf sea. P reaches complete equilibrium as soon as the deep ocean boxes become stably oxygenated. The timescales of evolution of O are slower and lay on the order of tens of millions of years (Lenton and Watson, 2000). Oxygen in the deep shelf overcomes hypoxia after the first few

millions of years and then slowly evolves towards equilibrium on the same timescale of O in the other ocean boxes. The dynamics of SedP_{org} is also strongly driven by level of oxygenation of the deep shelf sea.

Figure 3 of the revised manuscript is shown below:

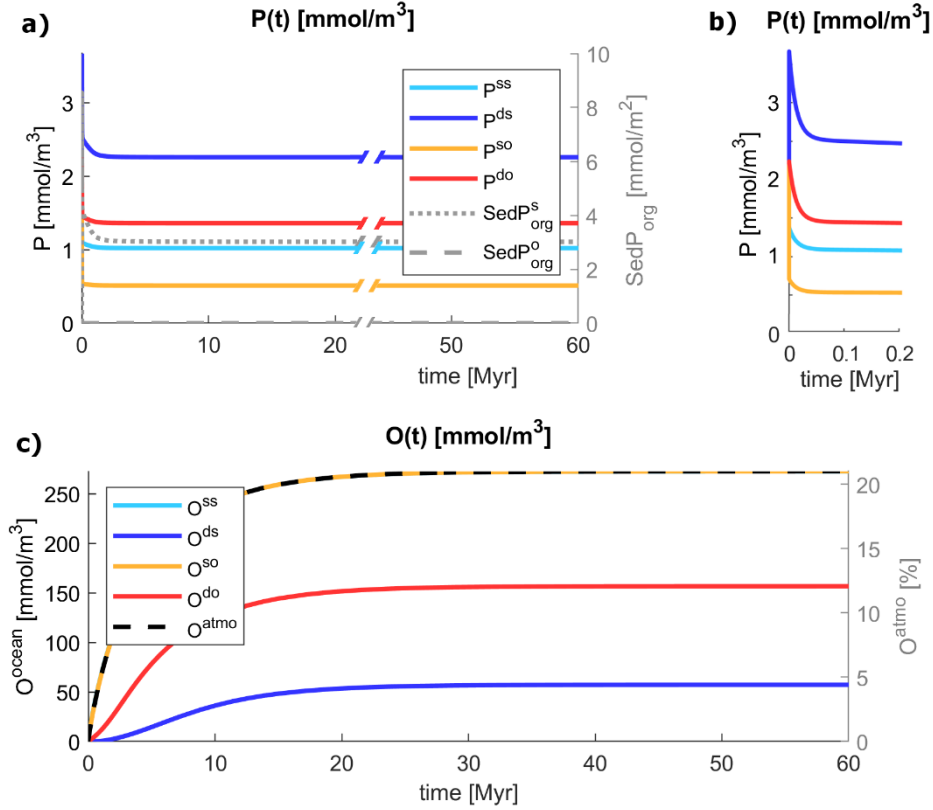


Figure 3: Evolution of the state variables from the initial conditions listed in Table 2 and remineralization lengths roughly in the middle of the interval of explored values: $z_{rem}^S = 20$ m, $z_{rem}^L = 250$ m. (a) Evolution of inorganic phosphorus P in the water column (left axis) and of organic phosphorus in the sediments $SedP_{org}$ (right axis); (b) zoom on the dynamics of P in the two hundred thousand years; (c) Evolution of oxygen in the water column (left axis) and atmosphere (right axis). In subplot (c) the two lines O^{ss} and O^{so} are overlapping: the two variables evolve closely due to the coupling of the surface ocean with the atmosphere via air-sea gas exchange.

Answer to Anonymous Referee nr.1

We thank Anonymous Referee nr.1 for their thoughtful comments which allowed us to improve the model and the manuscript. We especially appreciated the Referee's corrections regarding the benthic model and describe below our related changes to the code. We also provide a point by point answer to all of their comments. The Referee's comments are highlighted in blue, actual changes to the manuscript are highlighted in red.

R1C1)

The model for phosphorus (P) degradation in marine sediments considers aerobic respiration (Eq. 11) but seems to ignore anaerobic degradation. As a result the burial efficiency increases when oxygen is deleted in ambient bottom waters whereas the available observations show that P burial efficiency actually decreases under low-oxygen conditions (Slomp et al., 2002; Van Cappellen and Ingall, 1994; Wallmann, 2010). The authors should try to change their benthic model (i.e. include anaerobic degradation and enhanced P release under anoxia) or explain why they apparently ignore the strong evidence for enhanced benthic P release under low oxygen conditions.

We agree with Referee nr.1 that our model was failing at correctly representing the dependence of P degradation and burial on O₂ concentration, and have therefore modified the benthic model accordingly.

Our new model representation of the sediments includes an enhancement of the rate of P_{org} remineralization (+25%) and decrease of Ca-P burial (-50%) under anoxic conditions compared to oxic conditions, in line with Slomp & Van Cappellen 2007. The new equations are described in detail in subsections 2.2.4 and 2.2.5 of the revised paper, and can be read in full in the paper's appendix. The two new parameters determining changes in the rates of remineralization and Ca-P formation under anoxic conditions have been added to Table 4.

Despite these changes, our model results and conclusions regarding P and O₂ concentrations as a function of the particle remineralization lengths (Figure 4 and following ones) remain the same.

- New formulation of sediment P_{org} remineralization for the sediment box i overlaid by the deep ocean box j:

$$SedRem_{ox}^i = rm_r \cdot SedP_{org}^i \cdot (O^j / (O^j + K_O^s))$$

$$SedRem_{an}^i = (rm_r \cdot fe_{an}) \cdot SedP_{org}^i \cdot (1 - O^j / (O^j + K_O^s))$$

where fe_{an}=1.25 is the remineralization rate enhancement factor in anoxic conditions.

- New formulation of CaP formation for the sediment box i overlaid by the deep ocean box j:

$$CaPform_{ox}^i = CaP_r \cdot (SedP_{org}^i)^2 \cdot (O^j / (O^j + K_O^s))$$

$$CaPform_{an}^i = (CaP_r \cdot fs_{an}) \cdot (SedP_{org}^i)^2 \cdot (1 - O^j / (O^j + K_O^s))$$

where fs_{an}=0.5 is the Ca-P formation rate suppression factor in anoxic conditions.

The revised subsection 2.2.5 on sediment remineralization reads as follows:

In each sediment box i , remineralization of $SedP_{org}$ happens in a similar way to remineralization in the water column, with an aerobic and an anaerobic component. The first takes up oxygen from the overlaying deep-water box j and happens at a constant rate rm_r , while being limited by a Michaelis-Menten coefficient. Anaerobic remineralization releases its product to the atmosphere and happens at a faster rate $rm_r^* = rm_r \cdot fe_{an}$ with $fe_{an} > 1$, in agreement with recent observations and previous models (Slomp and Van Cappellen, 2006). Total sediment remineralization is therefore the sum of the two terms as in:

$$SedRem^i = rm_r \cdot SedP_{org}^i \cdot (O^j / (O^j + K_O^s)) + (rm_r \cdot fe_{an}) \cdot SedP_{org}^i \cdot (1 - O^j / (O^j + K_O^s)) \quad (11)$$

The revised subsection 2.2.4 on Ca-P formation reads as follows:

Ca-P formation happens at a lower rate under low oxygen conditions ($CaP_r^* = CaP_r \cdot fs_{an}$ with $fs_{an} < 1$), in agreement with observations and previous models (Slomp and Van Cappellen, 2006). The transition from aerobic and anaerobic conditions is controlled by a Michaelis-Menten type of function of the oxygen concentration in the deep ocean box j overlaying the sediment box i . The oxic and anoxic terms sum to the total formation term as in:

$$CaPform^i = (SedP_{org}^i)^2 \cdot [CaP_r \cdot O^j / (O^j + K_O^s) + (CaP_r \cdot fs_{an}) \cdot (1 - O^j / (O^j + K_O^s))] \quad (8)$$

R1C2)

The shelf model ignores P burial in shallow-water shelf sediments even though observations in the modern ocean indicate that most burial of particulate organic matter (POM) occurs in the inner shelf region at < 50 m water depth (Dunne et al., 2007). The authors should try to change their benthic model to include shallow shelf burial or explain why they ignore burial in shallow shelf regions.

We agree with Referee nr.1 that a significant fraction of the burial of POM happens in the shallowest regions of the shelf. Some of this is heavily influenced by the input of sediments and POM from the land. This shallowest portion of the shelf is also the most influenced by the details of the local bathymetry, tides, sediment resuspension and bottom layer mixing (Hill et al., 2008; Simpson and Pingree, 1978), which have important consequences in terms of physical-biogeochemical interactions. Differently from other models which distinguish between shallow (< 50 m deep) shelf and slope region (e.g., Slomp & Van Cappellen, 2007), BPOP calculates the sedimentation and burial fluxes dynamically, and would therefore require accounting for extra physical processes and flux parameterizations to justify going to such a higher level of detail. As our principal focus is on the first-order response to changes in the biological pump, we think that a 4-box representation of the ocean and of its circulation is a reasonable simplification, allowing us to keep the number of parameters small. We therefore keep this suggestion in mind for future developments of the model.

R1C3)

Small (slowly sinking) particles are mostly degraded in the water column whereas a substantial fraction of the large (rapidly sinking) particles is not degraded but deposited at the seafloor. Consequently, large POM particles reaching the seabed are more reactive (fresher) than small (older) particles and the kinetic constant for benthic degradation should increase with increasing particle size (Stolpovsky et al., 2018). Since particle size (sinking speed, mineralization length) is the major parameter varied in the modeling, the authors should try to consider this effect in their benthic model.

We thank Referee nr.1 for this interesting suggestion regarding the relation that may exist between the particles' remineralization rates in the sediments and their size or sinking speed. As BPOP allows to explore a variety of different hypothesis, we have decided to test the possibility of having sediment remineralization rates that depend on the particle properties, and we show our results below.

However, we highlight that the remineralization length z_{rem} (around which the model is built) does not only depend on the particles' sinking speeds, but also on the particles' remineralization rates in the water column. By this definition, it may not be given that particles that have larger remineralization lengths (our "large particles") have also larger sinking speeds. They may instead just be more refractory to water column remineralization, which also allows the particles to be remineralized on average more at depth. Other factors, such as the fact that large particles are defined as a secondary product of the coagulation of smaller particles can also influence the liability the LP_{org} pool. For these reasons we take this suggestion as a sensitivity experiment, but do not include it in the revised baseline model.

As a simple hypothesis, we have assumed that the sediment remineralization rate rm_r increases linearly with z_{rem} by 40% of our baseline value going from $z_{rem} = 0$ to $z_{rem} = 450$ m, with the baseline value of rm_r being found at $z_{rem}=225$ m, which is in the middle of the full range of explored values. In each run, the remineralization rate is calculated separately for small and large particles according to their respective z_{rem} . The two types of particles in the sediments are then solved separately and remineralized according to their respective rate. We have re-run the model under this assumption and include below a few significant comparison plots of the results of both our baseline run (the one adopted in the model) and the sensitivity run.

Our results show that there is no significant change in the model results that affects our primary conclusions from the baseline run. The main difference between the two sets of results consists in the facts that the sensitivity study shows a slightly stronger decoupling between the influence of the small and large particle remineralization lengths (respectively, z_{rem}^S and z_{rem}^L) on the equilibrium budgets and fluxes. The value of z_{rem}^S becomes even more influential for high z_{rem}^L , where the latter seems to make little difference in determining the equilibrium state of the model.

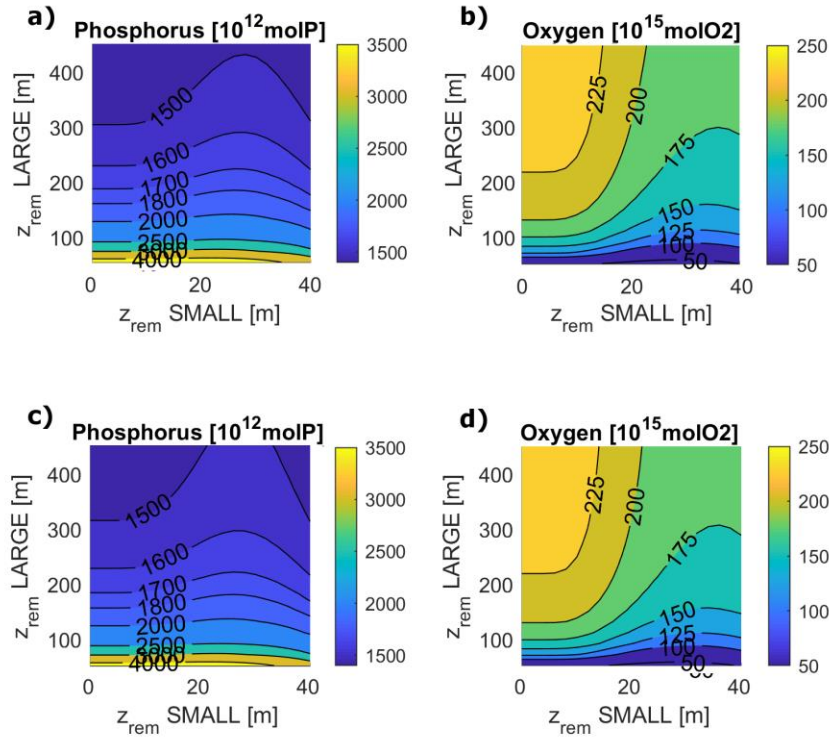


Figure R1-1: Ocean P and O_2 budgets for 2 model configurations: constant remineralization rate (subplots (a) and (b), new baseline); remineralization rate dependent on the particles' remineralization length (subplots (c) and (d)).

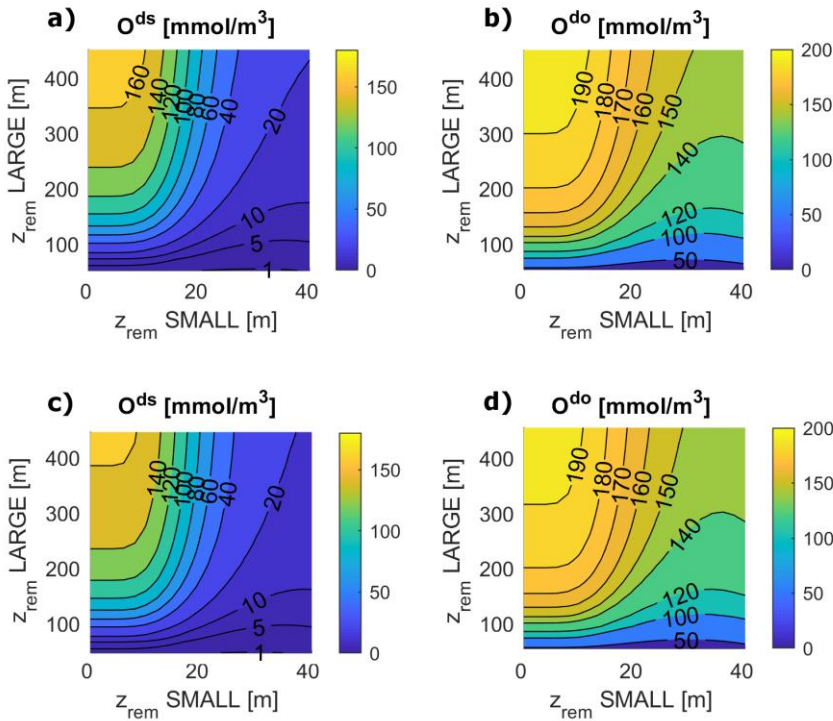


Figure R1-2: Oxygen concentrations in the deep shelf (ds) and in the deep open ocean (do) for 2 model configurations: constant remineralization rate (subplots (a) and (b), new baseline); remineralization rate dependent on the particles' remineralization length (subplots (c) and (d)).

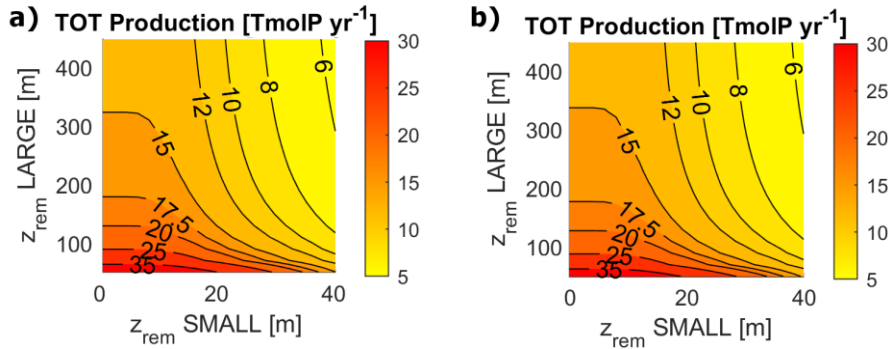


Figure R1-3: Total ocean production for 2 model configurations: constant remineralization rate (subplots (a) and (b), new baseline); remineralization rate dependent on the particles' remineralization length (subplots (c) and (d)).

We have also added the following paragraph to the discussion section, in subsection 5.1.3:

Furthermore, we have tested the impact of having sediment remineralization rates that vary with the particles' z_{rem} , under the assumption that the liability of small and large particles may be different. In our experiment, we increased the remineralization rm_r rate linearly with z_{rem} by 40 % of our baseline value (rm_r^0), with rm_r^0 being found at the centre of the interval of explored values of $z_{\text{rem}} = [0 \text{ m}, 450 \text{ m}]$. Under these conditions, we obtained a higher decoupling between the influence of z_{rem}^S and z_{rem}^L on budgets and fluxes, both being more strongly driven by the small particle properties for large values of z_{rem}^L .

R1C4)

Considering these model limitations, I do not know whether the authors' conclusion: "shelf ocean anoxia can coexist with an oxygenated deep ocean" (abstract, line 19) is really valid. Moreover, this conclusion depends on the model assumption that deep water formation takes place in the open ocean. This assumption is questionable since much of the modern deep water formation happens at continental margins. If these margin sites are oxygen depleted the resulting deep water would also be oxygen depleted.

We have changed the wording in the abstract to say that the results "suggest" this can happen (rather than "highlight" that it can) – the use of the word "can" should anyway have been taken to imply this is one of several possibilities. Regarding the impact of our representation of ocean circulation on the modelled oxygen distribution, in the modern ocean, deep water formation happens mostly at very high latitudes i.e., in the subpolar North Atlantic (Labrador Sea and Greenland Sea), in the Southern Ocean (Weddel Sea and Ross Sea). Both regions are characterized by physical and biogeochemical properties that differ substantially from our representation of a shelf sea, which is not intended to include polar and subpolar regions of sea-ice cover, continental ice shelves, deep convection etc. Therefore we don't think that attributing deep water formation to the shelf sea in our model would be the correct way to represent ocean circulation. Furthermore, our estimate of open ocean mixing and vertical exchange of water refers mostly to open ocean fluxes both at high and at low latitudes, and is in line with current estimates (Sarmiento and Gruber, 2006; Ganachaud and Wunsch, 2000). Instead it is our assumption of a circulation flux from the deep open ocean to the shelves, which thus boosts shelf nutrient concentration, which is more critical for determining the modelled oxygen distribution.

Bibliography (Answers to Anonymous Referee nr.1)

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Answer to Anonymous Referee nr.2

We thank Anonymous Referee nr.2 for their thoughtful comments and corrections which allowed us to fix some important typos in the manuscript and encouraged us to rethink about the way in which the model is implemented. We provide below a point by point answer to all of their comments. The referee's comments are highlighted in blue, while changes to the manuscript are highlighted in red.

R2C1)

It is stated on line 10 of page 4 that any organic matter that does not reach the sediments is instantaneously remineralised. This decision seems quite reasonable, but it is contradicted by the equations, in which organic matter is not only remineralized but is also advected and mixed. I recommend to do either one thing or the other but not both. If suspended particles are going to be mixed around in the model then they should have their own separate ordinary differential equations and state variables. Alternatively, if particle flux and remineralisation are made instantaneous, as stated in the manuscript, then there should be no mixing or advection of particulate organic matter. Whichever way it is done, the descriptions in the text need to be made consistent with the equations.

We thank Referee nr.2 for their observation, and we agree with them on the fact that our choice of combining an implicit sinking scheme with lateral advection and mixing can be troublesome. For this reason, we have modified the code in order to switch off the lateral advective and vertical mixing fluxes of POC. In our new baseline run, POC is exclusively redistributed throughout the boxes by vertical sinking, in line with the Referee's suggestion. In order to account for these changes in the model, we have modified the manuscript as described below.

The description of the P_{org} physical fluxes in section 2.2.2 has been reformulated as:

The implicit representation of the organic matter in the water column implies that no organic matter is accumulated in the ocean. In our baseline version of the model, corresponding to the results presented in this manuscript, SP_{org} and LP_{org} are redistributed throughout the watercolumn exclusively by implicitly modelled gravitational sinking before being either buried, accumulated in the sediments or remineralized. Even though the vertical export by downwelling and mixing (Stukel and Ducklow, 2017), and the lateral organic matter redistribution (Lovecchio et al., 2017; Inthorn et al., 2006) may be important when working with suspended SP_{org} ($z_{remS} = 0$), these fluxes are not currently accounted for in the model.

We have modified Figure 1 and 2 in order to account for this change in the model.

We have run the revised model both with and without the lateral advective and vertical mixing fluxes in order to understand the impact of removing these fluxes onto our model results. We include below a few significant plots which show overall higher oxygen levels and production in the absence of mixing/advective fluxes of P_{org} . Our main conclusions remain unchanged.

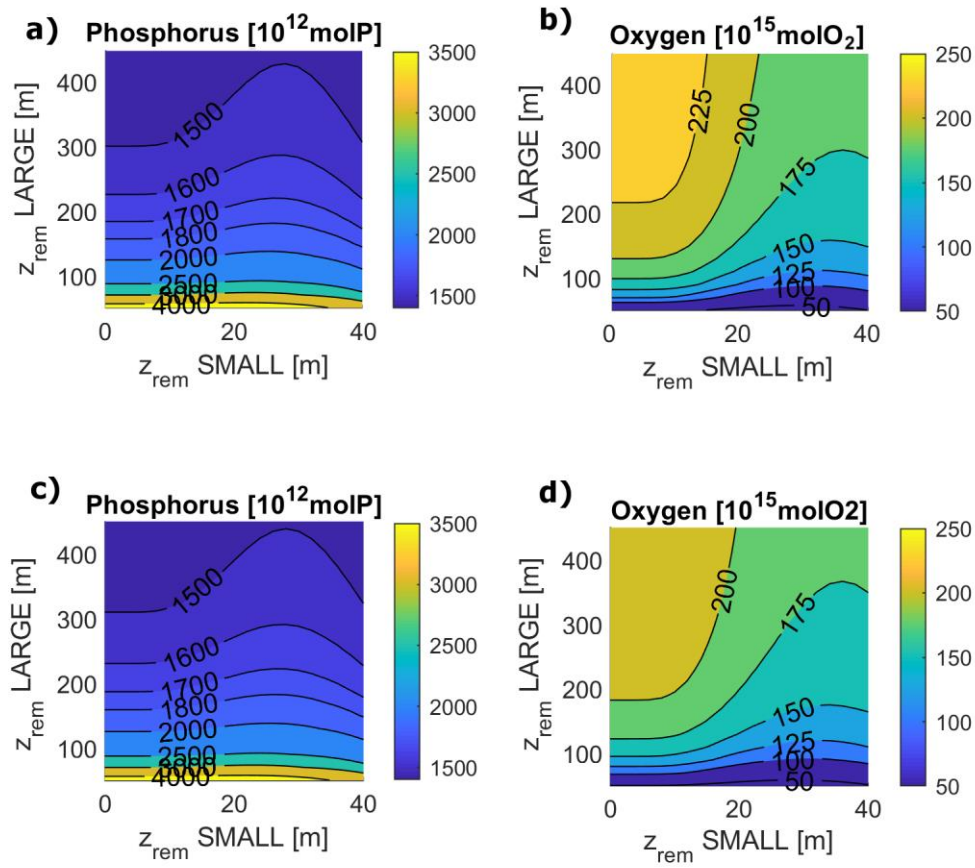


Figure R2-1: Ocean P and O_2 budgets for 2 model configurations: without POC lateral advection and vertical mixing (subplots (a) and (b), new baseline); with POC lateral advection and vertical mixing (subplots (c) and (d)).

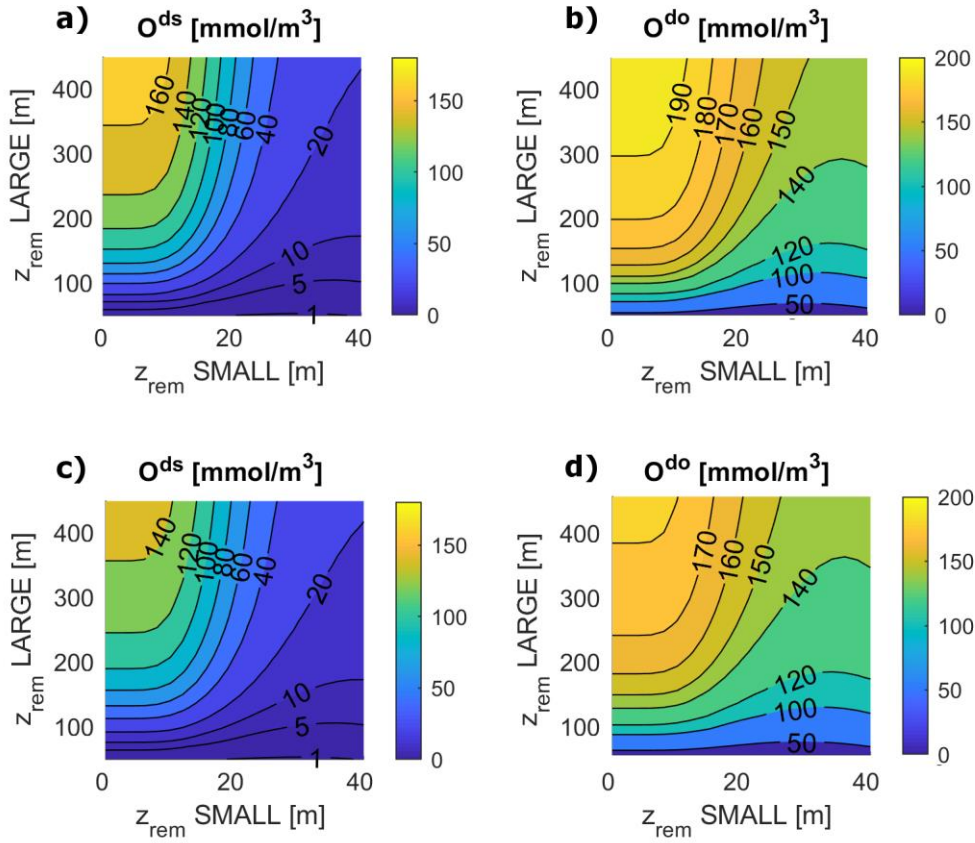


Figure R2-2: Oxygen concentrations in the deep shelf (ds) and in the deep open ocean (do) for 2 model configurations: without POC lateral advection and vertical mixing (subplots (a) and (b), new baseline); with POC lateral advection and vertical mixing (subplots (c) and (d)).

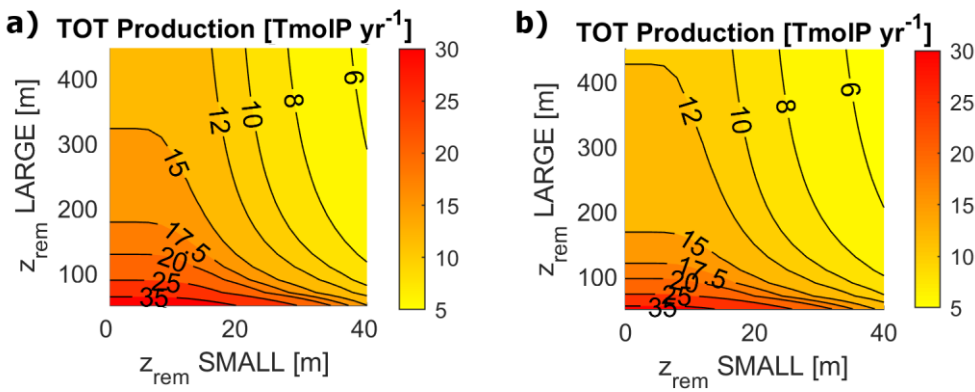


Figure R2-3: Total ocean production for 2 model configurations: without POC lateral advection and vertical mixing (subplots (a) and (b), new baseline); with POC lateral advection and vertical mixing (subplots (c) and (d)).

R2C2)

Tables 1 to 3 are very helpful. Another table needs to be added, listing the state variables in the model and stating their units. In addition, the units of all equations (the left-hand side) should also be stated, if they are not already given in the tables.

As suggested by Referee nr.2, we have added a table (**Table 1** of the revised manuscript) which indicates names and units of the state variables of the model.

Name	Description	Units
P^{ss}	Inorganic phosphorus in surface shelf sea box	mmol m^{-3}
P^{ds}	Inorganic phosphorus in deep shelf sea box	mmol m^{-3}
P^{so}	Inorganic phosphorus in surface open ocean box	mmol m^{-3}
P^{do}	Inorganic phosphorus in deep open ocean box	mmol m^{-3}
O^{ss}	Molecular oxygen in surface shelf box	mmol m^{-3}
O^{ds}	Molecular oxygen in deep shelf box	mmol m^{-3}
O^{so}	Molecular oxygen in surface open ocean box	mmol m^{-3}
O^{do}	Molecular oxygen in deep open ocean box	mmol m^{-3}
O^{at}	Oxygen mixing ratio in atmosphere (mol mol^{-1})	-
SedP_{org}^s	Organic phosphorus in the sediments of the shelf sea	mmol m^{-2}
SedP_{org}^o	Organic phosphorus in the sediments of the open ocean	mmol m^{-2}
P^{TOT}	Diagnostic variable: total P budget from sources and sinks only	Tmol P
O^{TOT}	Diagnostic variable: total O budget from sources and sinks only	Pmol O_2

Table 1: List of the model's state variables and of their units

We mention the new table in subsection 2.1 as follows:

The entire set of the model's state and diagnostic variables and their units are listed in Table 1.

R2C3)

Too many of the equations in the model are dimensionally inconsistent. That is to say, the units on the left-hand side of the equation do not match the units on the right-hand side of the equation when the different terms are combined together. As an example, equation 4 on page 4 is an equation for the rate of organic matter production in units of C2 GMDD Interactive comment Printer-friendly version Discussion paper phosphorus. This is a flux (rate of transfer), and therefore has to be in units of Moles y^{-1} or $\text{mmol m}^{-3} y^{-1}$ or similar. Because this is an ongoing flux rather than a one-off transfer, it must be expressed as a rate of transfer per unit time. However, none of the terms on the right-hand side of the equation have time anywhere in their units. The equation is formulated in such a way that it appears to be aimed at converting a fraction of the surface phosphorus concentration into production at each timestep, but the way it is actually formulated means that the rate of

conversion of surface phosphate into production (organic matter) will depend on the timestep used. Shorter time steps will convert phosphate to organic matter more rapidly than longer timesteps whereas ODE equations should be timestep-independent. Equation 5 is another example, where, according to the equation, 'Coag' must have units of organic matter concentration squared per year, which makes no sense. Before resubmission, I recommend that every equation in the model is checked for dimensional (units) consistency: multiplying through the units of the terms on the right-hand side should produce the units of the term on the left-hand side.

We thank Referee nr.2 for having spotted a few mistakes in the manuscript's equations. We have double checked the entire set of equations, the parameters' units and we have corrected a few typos.

As highlighted by the Referee, the uptake rate P_{eff} (Equation 4) as well as the coagulation factor c_g (Equation 5) were missing part of their units (see Table 4 of the revised manuscript). We have now corrected their units accordingly (see also Gruber et al., 2006). We have explained better the values and magnitudes of the parameters in the table's caption. We have also spotted another few inconsistencies in the units and fixed them both in the tables and in the equations.

R2C4)

I did not notice a statement anywhere that conservation of mass (or, more properly, conservation of total inventories of elements) has been checked and found to be stable. This is easy to do for a box model, whether it is closed or open. Obviously for a closed model, if there are no errors in the equations, the total sum of atoms of a given element should be constant over time. For an open model, the changes in the total inventory over time should exactly match the sum of external inputs over time minus the sum of the outputs from the system over time (i.e. $\Delta Inv = -$). This can easily be checked by adding two extra differential equations to the model: one to track the sum of the external inputs to the system and another to keep track of the sum of the losses from the system as a whole. From the model equations, I suspect that the model does not properly conserve phosphorus and oxygen but rather there is some (unintended) cumulative creation/destruction over time. This will interfere with the ability of the model to be run over long timescales to address the geological timescale questions of interest. It is a little bit unclear, but it appears that the amount of phosphate removed per unit time from the surface box as particle export is not identical to the amounts of phosphate added per unit time to the deep box and sediments combined. The euphotic zone depth appears in the equation for the former but not the latter, for instance, whereas if it appears in one then it should also appear in the other. Again, checks can be made by adding extra (book-keeping) ODEs to the model. For this example, one extra ODE could tally up the cumulative export from the surface box and another extra ODE could tally up the sum of the cumulative inputs to the deep and sediment boxes. At the end of each model run, a quick numerical check can be made to ensure that the tallies are identical within the precision of numerical rounding errors.

We agree with Referee nr.2 that a check on conservation of mass is essential for the model's evaluation. Even though we did not discuss it explicitly, our model does go to equilibrium on the long term, as now visible from **Figure 3** of the revised manuscript.

As a further check we have now added 2 extra variables to the model, P^{TOT} and O^{TOT} , which represent the total P and O budgets. These two variables (in units of TmolP and PmolO₂, respectively) are initialized to the total sum of the two tracers across all boxes at time zero.

At each time step, P^{TOT} and O^{TOT} evolve according to the sum of all sources and sinks in the model. Their derivatives are as follows:

$$\frac{dP^{TOT}}{dt} = \left[P_{in} - \left(CaPform^S \cdot A_{ocean} \cdot \mathcal{P}_{shelf} + CaPform^O \cdot A_{ocean} \cdot (1 - \mathcal{P}_{shelf}) \right) \right] \cdot 10^{-15}$$

$$\frac{dO^{TOT}}{dt} = \left[OProd^{ss} \cdot V^{ss} + OProd^{so} \cdot V^{so} \right. \\ \left. - \left((SedRemO^{ds} + AerRem^{ds}) \cdot V^{ds} + (SedRemO^{do} + AerRem^{do}) \cdot V^{do} \right. \right. \\ \left. \left. + OxyWeath \cdot (Mol_{atmo} \cdot 10^3) \right) \right] \cdot 10^{-18}$$

At the end of each model run we plot the sum of the total P and O content in the model at each time step by multiplying the concentrations in each box by the box volume or area (the latter for the sediments), and check that this corresponds to the time evolution of P^{TOT} and O^{TOT} calculated at run time regardless of the partition of the tracers among the boxes.

In order to include these new diagnostic variables in the model's description, we have modified the first paragraph of subsection 2.1 as follows:

The box model resolves explicitly for each relevant box the local concentrations of three types of tracers: molecular oxygen O_2 (O), inorganic dissolved phosphorus (P) and sediment organic phosphorus ($SedP_{org}$). The total budgets of P and O, respectively P^{TOT} and O^{TOT} , are also independently integrated from the net sources and sinks of the two tracers over the entire model domain, for the purpose of checking mass conservation.

We have also added the following statement to subsection 3.1 of the model evaluation:

Starting from the initial values listed in Table 3, the modelled state variables evolve towards equilibrium for any couple of values of z_{rem}^S and z_{rem}^L in the explored interval. Simple mass conservation checks show no hidden source or sink of tracers in the model's boxes.

We include below the result for the choice of z_{rem}^S and z_{rem}^L used for Figure 3 of the revised paper.

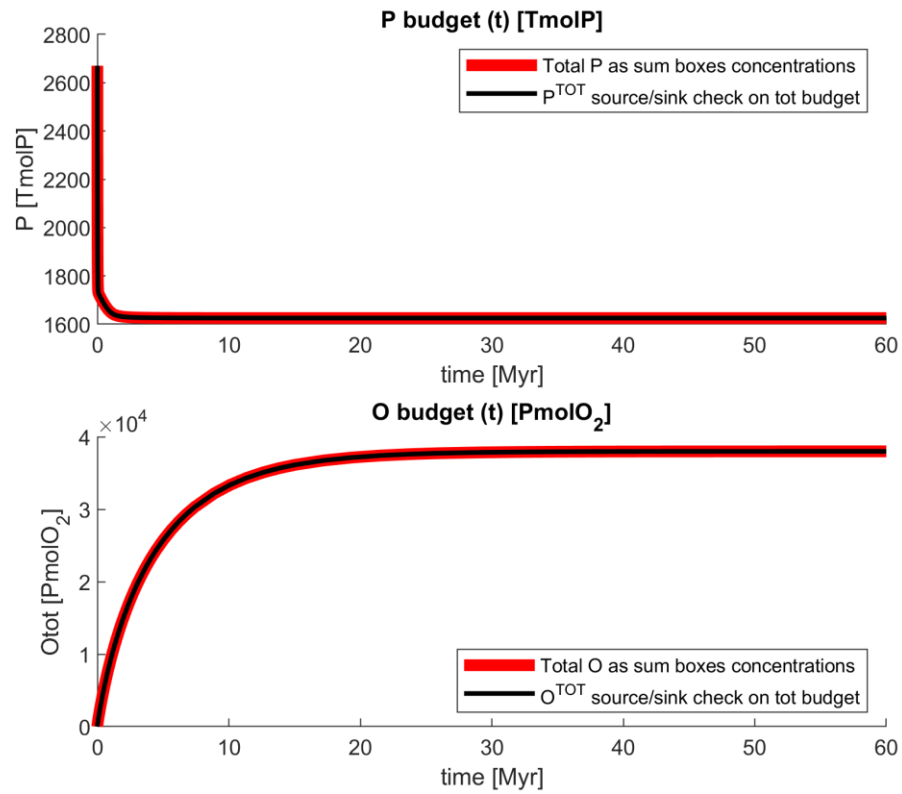


Figure R2-4: Comparison between the evolution of the total tracer budgets (P^{TOT} and O^{TOT}) calculated at run time from the tracer's net input fluxes (total sources + total sinks), and the tracer budgets calculated integrating the local concentrations in the boxes at each time step from the model's output.

BPOP-v1 model: exploring the impact of changes in the biological pump on the shelf sea and ocean nutrient and redox state

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Abstract. The ocean's biological pump has changed over Earth history from one dominated by prokaryotes, to one involving a mixture of prokaryotes and eukaryotes with trophic structure. Changes in the biological pump are in turn hypothesised to have caused important changes in the ocean's nutrient and redox properties. To explore these hypotheses, we present here a new box model including oxygen (O), phosphorus (P) and a dynamical biological pump. Our Biological Pump, Oxygen and Phosphorus (BPOP) model accounts for two – small and large – organic matter species generated by production and coagulation, respectively. Export and burial of these particles are regulated by a remineralization length (z_{rem}) scheme. We independently vary z_{rem} of small and large particles in order to study how changes in sinking speeds and remineralization rates affect the major biogeochemical fluxes, and O and P ocean concentrations. Modelled O and P budgets and fluxes ~~lie reasonably~~ close to present estimates for z_{rem} in the range of currently measured values. Our results highlight that relatively small changes in z_{rem} of the large particles can have important impacts on the O and P ocean availability and support the idea that an early ocean dominated by small particles was nutrient rich due to inefficient removal to sediments. The results also ~~highlight-suggest~~ that ~~extremely low oxygen concentrations in the shelf~~ ~~shelf ocean~~ ~~anoxia~~ can coexist with an oxygenated deep open ocean for realistic values of z_{rem} , especially for large values of the small particle z_{rem} . This could challenge conventional interpretations that the Proterozoic deep ocean was anoxic, which ~~are-are~~ derived from shelf and slope sediment redox data. This simple and computationally inexpensive model is a promising tool to investigate the impact of changes in the organic matter sinking and remineralization rates as well as changes in physical processes coupled to the biological pump in a variety of case studies.

1 Introduction

The 'biological pump' describes the production of organic matter at the ocean's surface (an oxygen source), its downward export/sinking flux, remineralisation at depth (an oxygen sink), and burial. This set of processes acts against the homogenization of tracer concentrations by the ocean's circulation, maintaining large-scale tracer gradients (Sarmiento and Gruber, 2006). In today's world, the biological pump plays a key role in transferring carbon from the atmosphere/surface ocean to the deep ocean and in so doing lowers atmospheric CO_2 and creates oxygen demand in deeper waters (Lam et al., 2011; Kwon et al., 2009). Those deeper waters with the greatest oxygen demand relative to oxygen supply can be driven hypoxic ($\text{O}_2 < 60 \text{ mmol m}^{-3}$), suboxic ($\text{O}_2 < 5 \text{ mmol m}^{-3}$) or even anoxic – as is being seen in parts of the ocean today (Keeling et al., 2010). By combining surface oxygen production and organic carbon burial, the biological pump plays a role in determining the long-term source of

oxygen to the atmosphere. The biological pump also provides a means of efficiently transferring organic matter and the nutrients it contains to marine sediments, if sinking through the water column happens fast enough compared to remineralization for the material to hit the bottom (Sarmiento and Gruber, 2006). Hence the biological pump plays a key part in balancing the input of phosphorus to the ocean with a corresponding output flux of phosphorus buried in marine sediments.

Through Earth's history, the characteristics, efficiency and impact of the biological pump are thought to have changed dramatically due to the evolution of increasingly large and complex marine organisms (Ridgwell, 2011; Logan et al., 1995; Boyle et al., 2018). Life in the ocean began as just prokaryotes, presumably attacked by viruses, with slow sinking of the resulting tiny particles. Now the marine ecosystem is a mix of prokaryotic cyanobacteria and heterotrophs, and size-structured eukaryotic algae, mixotrophs and heterotrophs all the way up to large jellyfish, fish and whales. Some of the resulting particles sink very fast (McDonnell and Buesseler, 2010). How changes in the biological pump have affected ocean nutrient and redox state at different times in Earth history is a subject of active research and hypothesis generation. Previous work has highlighted the Neoproterozoic Era, spanning from 1,000 to 541 million years ago, as of particular interest because it saw a shift of dominance from prokaryotes to eukaryotes and a series of dramatic shifts in the climate, biogeochemical cycling and ocean redox state (Katz et al., 2007; Brocks et al., 2017). A common paradigm has been to assume that a progressive rise of oxygen in the atmosphere (of uncertain cause) drove the oxygenation of the deep ocean at this time through air-sea gas exchange and mixing, but equally increases in the efficiency of the biological pump could have lowered ocean phosphorus concentration and thus oxygenated the ocean (Lenton et al., 2014). Recent data show a series of transient ocean oxygenation events ~660-520 Ma, which get more frequent over time, suggesting a complex interplay of processes on multiple timescales, including changes in the biological pump and ocean phosphorus inventory (Lenton and Daines, 2018).

During the Phanerozoic Eon there have been further changes to the biological pump. In particular, a rise of eukaryotic algae from the early Jurassic onwards is hypothesised to have increased the efficiency of the biological pump and thus oxygenated shallow waters (Lu et al., 2018), but presumably deoxygenated deeper waters, at least in the short term. In the oceanic anoxic events (OAEs) that occurred during the Mesozoic Era there were major increases in prokaryotic nitrogen fixation yet evidence for a eukaryote-dominated biological pump (Higgins et al., 2012), raising interesting questions as to whether this reinforced anoxia at depth.

Previous modelling work has examined the impact of changes in the organic matter remineralisation length/depth (z_{rem}) in the 3D GENIE intermediate complexity model (Meyer et al., 2016; Lu et al., 2018). Both studies clearly demonstrated the important control of the z_{rem} on ocean oxygen concentrations – as it gets larger the oxygen minimum zone shifts to greater depths. Furthermore, Lu et al. (2018) showed that an increase in z_{rem} can explain an observed deepening of the oxycline from the Paleozoic to Meso-Cenozoic in the ocean redox proxy I/Ca. However, coarse 3D models such as GENIE do not really resolve shelf seas and their dynamics, which are distinct from those of the open ocean. Furthermore, GENIE only accounts for one organic carbon species, overlooking processes of transformation of organic material, such as coagulation and fragmentation, which contribute to modulate the efficiency of the organic matter vertical export and burial (Wilson et al., 2008; Karakaş et al., 2009; Boyd and Trull, 2007).

In this study, we take a more idealised approach, exploring how changes in the properties of the biological pump may have affected the shelf sea and open ocean nutrient and redox state using a new Biological Pump, Oxygen

and Phosphorus (BPOP) box model. This model combines a box representation of the marine O and P cycles with an intermediate complexity representation of the biological pump transformations, including two classes of particulate organic matter (POM). BPOP allows us to modify the properties of two POM pools, whose abundance is regulated by the processes of production and coagulation. We focus on changes in the characteristic depths at which the two POM pools are remineralized, i.e., the particle remineralization length scale (z_{rem}), and study the resulting equilibrium budgets and fluxes. In the following sections we describe the model, we provide an evaluation of its performance in the context of modern observations and flux estimates, and finally present and discuss our model results.

2 Model description

Here we describe the Biological Pump, Oxygen and Phosphorus (BPOP) model. The model was implemented using Matlab and the equations are solved by the built-in ode15s solver. BPOP can easily run on a single core, integrating 50 million years of time in less than a minute on an ordinary machine, and is therefore computationally efficient. We refer to the user's manual (see the supplementary material) for further information on how to run the model.

2.1 Variables and circulation

The box model resolves explicitly for each relevant box the local concentrations of three types of tracers: molecular oxygen O_2 (O), inorganic dissolved phosphorus (P) and sedimented organic phosphorus ($SedP_{org}$). The total budgets of P and O, respectively P^{TOT} and O^{TOT} , are also independently integrated from the net sources and sinks of the two tracers over the entire model domain, for the purpose of checking mass conservation. The entire set of the model's state and diagnostic variables and their units are listed in Table 1. In the following subsections we describe the box model's geometry and discuss the physical and geochemical fluxes that drive the tracers' dynamics. Box properties are listed in Table 24, while the set of parameters adopted for the modelled physical and geochemical fluxes can be found in Table 32.

2.1.1 Box properties and physical fluxes of inorganic tracers

The box model includes 4 ocean boxes, 1 atmospheric box and 2 sediment boxes (Figure 1a). The ocean and sediment boxes are equally split between shelf sea and open ocean, both including one surface ocean box and one deep ocean box.

O and P are exchanged between the 4 ocean boxes through advection and mixing, including an fundamental upwelling recirculation between shelf sea and open ocean (Wollast, 1998). For a generic tracer concentration C and in the i^{th} box, the physical exchange flux is represented by

$$AdvMix(C)^i = \sum_j MassFlux_{ij}/V^i \cdot (C_j - C_i) \quad (1)$$

For each surface box i , air-sea gas exchange allows O fluxes between the ocean and the atmosphere (at). The flux is positive when directed into the ocean and depends on the gas transfer velocity K_w and Henry's constant K_{Henry} , as in:

$$AirSea^i = K_w \cdot (O^{at}/K_{Henry} - O^i) \cdot A^i/V^i \quad (2)$$

where K_w is a function of the prescribed mean temperature T_{mean} and wind speed W_{speed} (Sarmiento and Gruber, 2006).

2.1.2 Initialization and boundary fluxes

The model is initialized with an even concentration of P (P_{ini}) in all the ocean boxes, zero oxygen and zero sediment P_{org} . A constant input of P from rivers (P_{in}) into the surface ocean replenishes the P ocean reservoir despite the burial flux (net sink of P_{org}) into the sediments. P_{in} is in part delivered directly to the surface open ocean (Sharples et al., 2017). At equilibrium, the P_{org} burial flux ~~must~~ balances P_{in} . Oxidative weathering determined by atmospheric ~~oxygen~~ O^{at} constitutes a net sink flux for O. The weathering flux depends on a constant a baseline flux W_0 and it scales like the square root of the oxygen concentration normalised to present values O_{mix_0} (Lenton et al., 2018), following:

$$OxyWeath = W_0 \cdot \sqrt{O^{at}/O_{mix_0}} \quad (3)$$

2.2 Biological pump details

The modelled tracer cycles are coupled by a set of biological transformations, i.e., the biological pump, governing the cycle of production, remineralization and burial of P_{org} in the water column and in the sediments. P_{org} in the water column is resolved implicitly: at each time step all the produced P_{org} that does not reach the sediments is instantaneously remineralized. In this sense, in our model no P_{org} can accumulate in the ocean's water column. This scheme is like the one used to represent detrital POM in some modern ocean biogeochemical models (Moore et al., 2004). P and O biological fluxes are coupled by a fixed Redfield ratio OP_{Red} . The next few paragraphs describe the cycle of production, coagulation, export, remineralization and burial that constitute the biological pump representation. The full set of parameters used to resolve the P_{org} cycle is provided in Table 43.

2.2.1 Particle classes, production and coagulation

The model includes two P_{org} classes, which get produced, exported and remineralized in the ocean's water column: small P_{org} (SP_{org}) and large P_{org} (LP_{org}). The use of two P_{org} classes is in line with modern ocean in situ observations, which reveal a bimodal distribution of the particle sizes and sinking speeds (Riley et al., 2012; Alonso-González et al., 2010). Moreover, it allows to better reproduce the commonly observed Martin power-law decay of the particle export flux with the use of a remineralization length scheme of export and burial fluxes (Boyd and Trull, 2007).

Organic matter production happens only in the surface ocean boxes through the uptake of P. This is regulated by a maximum rate P_{eff} and a Michaelis-Menten kinetics with constant K_p . Production in each i^{th} box only generates SP_{org} , according to:

$$Prod^i = P_{eff} \cdot (P^i / (P^i + K_p)) \cdot P^i \quad (4)$$

LP_{org} is generated via the coagulation of SP_{org} either at the surface after production or at depth after the export of SP_{org} from the surface. The coagulation of SP_{org} into LP_{org} in each box i is proportional to the square of the local SP_{org} concentration and is regulated by a coagulation rate cg_r (Boyd and Trull, 2007; Gruber et al., 2006), as in:

$$Coag^i = cg_r \cdot (SP_{org}^i)^2 \quad (5)$$

Coagulation impacts the relative contribution of small and large particles to the export and burial fluxes by subtracting from the local SP_{org} pool and adding to the LP_{org} pool.

2.2.2 Physical fluxes of organic material

The implicit representation of the organic matter in the water column implies that no organic matter is accumulated in the ocean. In our baseline version of the model, corresponding to the results presented in this manuscript, SP_{org} and LP_{org} are redistributed throughout the watercolumn exclusively by implicitly modelled gravitational sinking before being either buried, accumulated in the sediments or remineralized. Even though the ~~However, the model allows to include lateral advective and vertical mixing fluxes of organic phosphorus by setting to one the value of the parameter , which acts as a switch in the equations. This may be necessary when working with suspended SP_{org} pools ($z_{rem}^S = 0$), and therefore that modelled SP_{org} and LP_{org} can only be transported by physical fluxes from regions of production to regions of remineralization. For this reason, physical fluxes affect the two organic matter species only in a single direction (Figure 1b). Despite this limitation, we believe that , as including the influence of these physical fluxes on the water column P_{org} is essential to account for both the vertical organic matter export by advective downwelling and mixing (Stukel and Ducklow, 2017), and the lateral organic matter redistribution from the coast to the open waters both at the surface and at depth (Lovecchio et al., 2017; Inthorn et al., 2006); may be important when working with suspended SP_{org} ($z_{rem}^S = 0$), these fluxes are not currently accounted for in the model. When advected and mixed, implicitly modelled SP_{org} and LP_{org} can only be transported by physical fluxes from regions of production to regions of remineralization. For this reason, if included, these fluxes affect the two organic matter species only in a single direction (Figure 1b). Due to the wide extension of the modelled ocean boxes, lateral fluxes are assumed to only affect SP_{org} . The lateral export of SP_{org} reduces its availability for export and burial in the shelf sea, i.e., at each time step lateral fluxes out of the shelf happen before the SP_{org} vertical export and sedimentation fluxes are calculated.~~

2.2.3 Remineralization length scheme

The export and sedimentation fluxes of P_{org} through the water column are represented by a remineralization length scheme. In this representation, the vertical fluxes of organic matter $f(z)$ vary exponentially with depth. The shape of the exponential depends on the value of the remineralization length (z_{rem}) of each organic matter species:

$$f^k(z) = f_0^k \cdot e^{-\frac{z-z_0}{z_{rem}^k}}, \quad (6)$$

where f_0^k is the flux at the reference depth z_0 , and the index k indicates the organic matter pool of reference, either small (S) or large (L). This representation of the export flux is convenient, as it does not depend on the specific choice of z_0 (Boyd and Trull, 2007).

The remineralization length z_{rem} indicates the distance through which the particle flux becomes 1/e times (about 36 %) the flux at the reference depth (Buesseler and Boyd, 2009; Marsay et al., 2015). This quantity is expressed in metres and can be calculated as the ratio between the particle sinking speed and the particle's remineralization rate (Cavan et al., 2017). Consequently, z_{rem} implicitly contains information on several particle inherent properties (among which density, size, shape, organic matter liability) as well as information about the surrounding environment, e.g., the type of heterotrophs which feed upon the organic material (McDonnell and Buesseler, 2010; Baker et al., 2017). For simplicity, we assume that the remineralization length of small and large particles does not vary between shelf sea and open ocean boxes. We examine the potential impact of this limitation in the discussion section of the paper.

2.2.4 Sediments and burial

SP_{org} and LP_{org} accumulate in the sediments as SedP_{org}, which is calculated as a density per unit of area. The sediment flux into the sediment box *i* depends on the organic matter concentration in the overlaying deep ocean box *j* and on the remineralization length of the two pools as in:

$$5 \quad \text{SedFlx}^i = (\text{SP}_{org}^j \cdot \exp(-\Delta Z_j / z_{rem}^S) + \text{LP}_{org}^j \cdot \exp(-\Delta Z_j / z_{rem}^L)) \cdot \Delta Z_j \quad (7)$$

The accumulated SedP_{org} is partially slowly remineralized and partially irreversibly buried in a mineral form. Phosphorus burial as mineral Ca-P- is modelled as a function of the square of SedP_{org} that accumulates in the sediments, in a way that is analogous to the dynamics of particle coagulation, and is regulated by a constant rate coefficient CaP_r. Ca-P formation happens at a lower rate under low oxygen conditions (CaP_r^{*} = CaP_r · f_{san} with f_{san} < 1), in agreement with observations and previous models (Slomp and Van Cappellen, 2006). The transition from aerobic and anaerobic conditions is controlled by a Michaelis-Menten type of function of the oxygen concentration in the deep ocean box *j* overlaying the sediment box *i*. The oxic and anoxic terms sum to the total formation term as in:

$$10 \quad \text{CaPform}^i = (\text{SedP}_{org}^i)^2 \cdot [\text{CaP}_r \cdot O^j / (O^j + K_O^S) + (\text{CaP}_r \cdot f_{san}) \cdot (1 - O^j / (O^j + K_O^S))] \quad \text{CaP}_r \cdot (\text{SedP}_{org}^i)^2 \quad (8)$$

This flux is essential to balance the continuous P river input, therefore preventing the ocean from overflowing with nutrients.

2.2.5 Remineralization in the water column and sediments

At each time step, remineralization in the water column completely depletes the P_{org} that has not reached the sediments. In the two surface boxes, remineralization of P_{org} that is not exported below the euphotic layer uses up part of the oxygen that was released by production. For this reason, net oxygen production in each surface box is proportional to the export of P_{org} below the euphotic layer. Export from a surface box *i* to a deep box *j* happens both via gravitational sinking and via mixing, as in:

$$25 \quad \begin{aligned} \text{VExp}^i &= \text{SP}_{org}^i \cdot \exp(-(\Delta Z_{eu}/2) / z_{rem}^S) + \text{LP}_{org}^i \cdot \exp(-(\Delta Z_{eu}/2) / z_{rem}^L) \quad (9) \\ \text{VExp}^i &= \text{SP}_{org}^i \cdot \exp(-(\Delta Z_{eu}/2) / z_{rem}^S) + \text{LP}_{org}^i \cdot \exp(-(\Delta Z_{eu}/2) / z_{rem}^L) + \\ &\quad \frac{(\text{SP}_{org}^i + \text{LP}_{org}^i) \cdot \text{Mix}_{ij}}{\text{V}^i} \quad (9) \end{aligned}$$

At depth, the remineralization of P_{org} that does not reach the sediments happens through both aerobic and anaerobic processes, completely depleting the remaining P_{org}. Water-column remineralization of P_{org} into inorganic P in the deep box *j* is therefore calculated as:

$$30 \quad \text{WcRem}^j = \text{SP}_{org}^j \cdot (1 - \exp(-\Delta Z_j / z_{rem}^S)) + \text{LP}_{org}^j \cdot (1 - \exp(-\Delta Z_j / z_{rem}^L)) \quad (10)$$

In each deep ocean box *i*, aerobic remineralization uses some of the available oxygen and is therefore limited by a Michaelis-Menten kinetics with a half-saturation constant K^w_O (DeVries and Weber, 2017). Anaerobic remineralization takes up the entire remaining P_{org} that is not remineralized aerobically and releases a product which “bubbles up” to the atmosphere, reacting with atmospheric oxygen. In our model, the reducing agent produced by anaerobic remineralisation is methane gas and it is only produced when the sediments and the deep shelf water column have gone anoxic. As we do not track other oxidising agents such as SO₄ there is nothing for the methane to be oxidised by until it reaches the surface ocean, and as the surface ocean is equilibrated with the atmosphere, the fact that we assume oxidation in the atmosphere is a reasonable approximation.

In each sediment box i , ~~aerobic~~ remineralization of $SedP_{org}$ ~~happens in a similar way to remineralization in the water column, with an aerobic and an anaerobic component. However, remineralization in the sediments is not instantaneous, but happens at a fixed rate which depends on the oxygenation state of the overlaying water column. Aerobic remineralization~~ takes up oxygen from the overlaying deep-water box j and happens at a ~~constant~~ rate rm_r , while being ~~which is~~ limited by a Michaelis-Menten coefficient, ~~analogously to aerobic remineralization in the deep water column. Anaerobic remineralization releases its product to the atmosphere and happens at a faster rate $rm_r^* = rm_r \cdot fe_{an}$ with $fe_{an} > 1$, in agreement with recent observations and previous models~~ (Slomp and Van Cappellen, 2006). ~~Total sediment remineralization is therefore the sum of the two terms as in~~ This flux is regulated by a constant remineralization rate coefficient rm_r as in:

$$SedRem^i = rm_r \cdot SedP_{org}^i \cdot (O^j / (O^j + K_O^s)) + (rm_r \cdot fe_{an}) \cdot SedP_{org}^i \cdot (1 - O^j / (O^j + K_O^s)) \quad (11)$$

2.3 Equations summary

The dynamics of the model's 11 state variables is regulated by just as many equations. We summarize here the major terms for P, O and $SedP_{org}$ in the surface ocean (s), deep ocean (d), atmosphere (at) and sediments, without distinguishing between coastal and open ocean boxes and assuming that all terms have been scaled with the reference box' dimensions. A full set of equations including the explicit formulation of all the flux terms for each box can be found in the paper's Appendix.

$$\frac{dP^s}{dt} = P_{in} + AdvMix(P)^s - VExp, \quad (12)$$

$$\frac{dP^d}{dt} = AdvMix(P)^d + WcRem + SedRem \quad (13)$$

$$\frac{dO^s}{dt} = AdvMix(O)^s + VExp \cdot OP_{Red} + AirSea \quad (14)$$

$$\frac{dO^d}{dt} = AdvMix(O)^d - WcRem_{Aer} \cdot OP_{Red} - SedRem_{Aer} \cdot OP_{Red} \quad (15)$$

$$\frac{dSedP_{org}}{dt} = SedFlx - CaPform - SedRem \quad (16)$$

$$\frac{dO^{at}}{dt} = -\sum AirSeaFlx - WcRem_{Ana} \cdot OP_{Red} - SedRem_{Ana} \cdot OP_{Red} - OxyWeath \quad (17)$$

Where: P_{in} is the river input of P to the ocean's surface, AdvMix indicates the advective and mixing physical fluxes of the variable of interest (which differ for each box according to the circulation scheme); Exp is the export flux of P_{org} in P units; WcRem indicates the water column complete remineralization of the organic material in P units, which is split into an anaerobic (Ana) and aerobic (Aer) component; SedRem indicates the sediment remineralization of $SedP_{org}$ in P units (also aerobic and anaerobic); AirSeaFlx represents the air-sea flux exchange of O; OxyWeath is the O weathering flux sink; SedFlx is the $SedP_{org}$ accumulation flux as regulated

by the remineralization length scheme at the bottom of the water column; and finally CaPform represents the sediment burial flux of P in mineral form. For each box, flux terms are rescaled with the appropriate box geometry.

2.4 Strategy: sensitivity studies for varying z_{rem}

In order to characterize the model, we analyse the equilibrium budgets and fluxes of the state variables for varying z_{rem} values separately for SP_{org} and LP_{org} , respectively $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$. We adopt a range of z_{rem} values that fall close to modern observations (Cavan et al., 2017; Buesseler and Boyd, 2009; Marsay et al., 2015) and keeps into consideration our future aim to apply the model to simulate the impact of the time evolution of the early biological pump (at the Neoproterozoic-Palaeozoic transition). For this reason, we don't push the range as far as what would be needed to consider the impact of fast sinking rates typical of silicified or calcified small phytoplankton (McDonnell and Buesseler, 2010; Lam et al., 2011). In our sensitivity simulations, $z_{\text{rem}}^{\text{S}}$ is in the range of [0, 40 m], while $z_{\text{rem}}^{\text{L}}$ varies in the range of [50 m, 450 m].

3 Evaluation

3.1 Timescales

Starting from the initial values listed in Table 3, the modelled state variables evolve towards equilibrium for any couple of values of $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ in the explored interval. Simple mass conservation checks show no hidden source or sink of tracers in the model's boxes. Figure 3 illustrates an example of evolution of the variables for $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ in the middle of the interval of explored values for both particle types. In all the ocean boxes, P shows an initial oscillation that evolves on timescales of tens of thousands of years (Figure 3a,b), as expected by the typical timescale of evolution of the tracer (Lenton and Watson, 2000). This is followed by a slower drift which depends on the dynamics of the deep water oxygen content, as the release and burial of P in the sediments depends on the level of oxygenation of the deep ocean and especially of the deep shelf sea. P reaches complete equilibrium as soon as the deep ocean boxes become stably oxygenated. The timescales of evolution of O are slower and lay on the order of tens of millions of years (Lenton and Watson, 2000). Oxygen in the deep shelf overcomes hypoxia after the first few millions of years and then slowly evolves towards equilibrium on the same timescale of O in the other ocean boxes. The dynamics of SedPorg is also strongly driven by level of oxygenation of the deep shelf sea.

3.2 Modern ocean budgets and fluxes

Modern estimates of the $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ vary depending on the region of sampling and on the local community structure, with most of the measurements focusing on large or heavy particles and most studies focusing on the open ocean (Iversen and Ploug, 2010; Cavan et al., 2017; Lam et al., 2011). Furthermore, only a very limited number of measurements accounts for both microbial and zooplankton remineralization, the latter disregarded by lab measurements of z_{rem} (Cavan et al., 2017). Considering the fundamental role of the shelf sea in our model (always accounting for > 98 % of the total burial), we evaluate modelled tracer budgets and fluxes for values of $z_{\text{rem}}^{\text{L}}$ that lay around 76 m, as measured in situ by Cavan et al. (2017) for a modern shelf sea. We pose no restrictions on $z_{\text{rem}}^{\text{S}}$ due to the lack of precise measurements. A summary of our evaluation is provided in Table 5.

In ~~the this~~ above mentioned range of z_{rem} , model results are lower but in the same order of magnitude of current estimates for marine tracer budgets (Figure 3). Our model predicts equilibrium budgets of ~~about between 2500~~ 2500 TmolP and 2800 TmolP for phosphorus, and an oxygen budget of ~~between 100 PmolO₂ and 1450~~ 1450 PmolO₂ in the entire ocean, compared to the estimated total P reservoir of 3100 TmolP (Watson et al., 2017) and estimated ~~deep~~ ocean O₂ reservoir of ~~between 225~~ 220 PmolO₂ and 310 PmolO₂ (Slomp and Van Cappellen, 2006). (Keeling et al., 1993; Duursma and Boisson, 1994). Due to the relative size of the ocean boxes, it is important to underline that total budgets are strongly driven by the deep open ocean budget, and that the low oxygen reservoir of our model may be connected to an underestimation of the deep open ocean oxygenation.

Deep shelf P and O concentrations lay in the ranges of [~~3.93~~ 5 mmol m⁻³, ~~5.44~~ 5 mmol m⁻³] and [~~32.8~~ mmol m⁻³, ~~12.3~~ 5 mmol m⁻³] respectively (Figure ~~5.64~~ 5). Deep shelf nutrient concentrations are higher than expected by about a factor of two compared to modern values, possibly due to the fact that our model does not store any P_{org} in the water column or due to an underestimation of the vertical supply of nutrients to the surface shelf (e.g., via mixing). Limiting deep P concentrations via lower remineralization or higher burial rates, however, also results in sensibly lower production rates. In the deep open ocean, P and O concentrations ~~fall in the ranges of shift to about 2.2~~ [2.0 mmol m⁻³, 2.3 mmol m⁻³] and ~~120~~ [72 mmol m⁻³, 110 mmol m⁻³] respectively, ~~with minor changes for varying z_{rem}^S .~~ For any combination of z_{rem}^S and z_{rem}^L , O levels in surface ocean boxes lay ~~around between 272.5 mmol m⁻³ and 274~~ 275 mmol m⁻³, a good approximation of average modern surface values (Garcia et al., 2018a). In general, the deep shelf always shows the highest P values and lowest O concentrations compared to the other ocean regions, while, as expected, the surface shelf sea is richer in P compared to the surface open ocean.

Modelled biological fluxes, such as production and export and burial, fall around the low end lower but of the same order of magnitude of present estimates (Figure 76). ~~This is possibly due to the elementary representation of production in our model, which does not account for explicitly for the influence of the microbial loop nor distinguishes between new and regenerated production. We find~~ Our model predicts an equivalent C primary production of between ~~1000~~ 18.8 TmolC GtC yr⁻¹ and ~~1800~~ 51.5 GtTmolC yr⁻¹, and an export below the euphotic layer ranges between 2.8 GtC yr⁻¹ and 4.0 GtC yr⁻¹, both calculated using a fixed C:P Redfield ratio of 106. These ~~is~~ must be compared to an expected value of ~~production of between at least 353~~ 300 GtTmolC yr⁻¹, ~~reaching up to more than 9000 TmolC yr⁻¹ according to satellite estimates and 80 GtC yr⁻¹ (Carr et al., 2006).~~ ~~E and an estimated export flux below the euphotic layer ranges between 250 TmolC yr⁻¹ and 300 TmolC yr⁻¹, compared to an estimated value that lays between of at least 4415 TmolC yr⁻¹ and 1660 TmolC yr⁻¹ (Henson et al., 2011).~~ ~~Even though~~ Despite the absolute ~~values of the fluxes are being at the low end of the present estimates lower than expected,~~ modelled export production (the export to production ratio) and the burial to production ratio compare well to range of present estimates, the relative magnitude of the fluxes compared to production lay in the range of present estimates. The modelled export corresponds to between ~~158~~ % and ~~353~~ 30 % of total production, strongly depending on z_{rem}^S , compared to an expected range of 2 % - 20 % (Boyd and Trull, 2007). Buried P_{org} corresponds to between ~~0.34~~ % and ~~0.98~~ % of total production, compared to an expected 0.4 % (Sarmiento and Gruber, 2006). In terms of the shelf contribution to the total fluxes, model results also fall close to present estimates. Modelled production in the surface shelf sea represents between ~~4412~~ % and ~~25~~ 0 % of total production (expected 20%) (Barrón and Duarte, 2015; Wollast, 1998). The fraction of modelled export and burial that happens in the shelf region represent, respectively, ~~about~~ [210 %, 27 %] and nearly 100 % of the total ocean fluxes, compared to estimated modern values of 29 % and 91 % (Sarmiento and Gruber, 2006). Our overestimation of the shelf

contribution to the burial fluxes may be due to the underestimation of the open ocean particles z_{rem} compared to observations (Cavan et al., 2017; Lam et al., 2011), ~~i.e. due to~~ our choice of using the same value of $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ for both the coastal and the open ocean box. This simplifying assumption limits the capacity of P_{org} to reach the deep sediment layer in the open ocean. We explore potential limitations of this choice in the Discussion section.

4 Results

4.1 Budgets and fluxes sensitivity to changes in z_{rem}

Around the lowest values of $z_{\text{rem}}^{\text{L}}$ adopted in the present study, i.e., in the range of [50 m, 100 m], our model shows a strong sensitivity of the total and local ocean P and O budgets for small changes of $z_{\text{rem}}^{\text{L}}$ (Figure 43). This is true for any $z_{\text{rem}}^{\text{S}}$, with minor differences between low and high $z_{\text{rem}}^{\text{S}}$ values. For smaller $z_{\text{rem}}^{\text{L}}$, the model shows a sharp increase in P concentrations in all the ocean boxes and a substantial decrease of O levels at depth (Figures 5.64, 5), which are coupled to high levels of production and remineralization and low rates of sedimentation (Figure 76). Essentially slow sinking and/or rapid remineralization results in inefficient removal of P to shelf sea sediments, requiring the ocean concentration of P to rise considerably for P output to balance (fixed) P input to the ocean.

Our model results show that for any couple of values of $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ in the entire explored range, the biological pump is able to oxygenate the surface ocean (surface O levels lay close to 27.32 mmol m⁻³) and, for most values, also to maintain the deep ocean above the level of hypoxia (Figure 65). The model shows a substantial difference between the deep shelf and the deep open ocean: while the latter is substantially oxygenated ($O > 50$ mmol m⁻³) for nearly any value of $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$, the deep shelf is hypoxic or even suboxic for a broad range of small values of $z_{\text{rem}}^{\text{L}}$, especially close to modern shelf $z_{\text{rem}}^{\text{L}}$ observations. Considering the wide spatial extension of our boxes, we expect these low oxygen levels to indicate the development of local anoxia in the deep shelf.

In a limited interval of small $z_{\text{rem}}^{\text{S}}$ values (roughly $z_{\text{rem}}^{\text{S}} < 6$ m), model results depend only on the LP_{org} properties due to the rather irrelevant contribution of SP_{org} to export and remineralization. For larger z_{rem} values ($z_{\text{rem}}^{\text{S}} > 6$ m and $z_{\text{rem}}^{\text{L}} > 100$ m), model results show a strong interdependence of equilibrium budgets and absolute fluxes on both $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$. Interestingly, in this range of values, ~~the ratio of export to~~ production depends nearly entirely on the small particle properties, ranging between 20.10 % for low $z_{\text{rem}}^{\text{S}}$ and 40.30 % for high $z_{\text{rem}}^{\text{S}}$, an overall trend that affects also the ratio of deep remineralization to surface production (Figure 76).

It is also important to notice that, for any couple of $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$, modelled tracer concentrations and fluxes fall in a range of values that never exceeds by orders of magnitude the modern observed values. Considering all of the ocean boxes, P concentrations vary in the range of roughly 0.3 mmol m⁻³ and 6.58 mmol m⁻³, while O levels lay between 1 mmol m⁻³ and 200 mmol m⁻³. Production in carbon units lays in the interval [6007.6 GtTmolC yr⁻¹, 220070.7 GtTmolC yr⁻¹].

4.2 Budgets and fluxes contribution by particle class

~~The 4.2 Budgets and fluxes contribution by particle class~~

~~The~~ relative role of small and large particles to modelled biological and physical fluxes depends on a combination of their inherent properties (z_{rem}) and of coagulation. Coagulation of SP_{org} into LP_{org} after production in surface boxes affects between 20.10 % and 50.40 % of the small particles in the surface shelf sea and between 5.3 % and

~~25~~20 % of the small particles in the surface open ocean (Figure ~~87~~a,b). The highest rates of coagulation of SP_{org} into LP_{org} in the surface ocean are found for especially high P concentrations resulting in high rates of small particle production. Rates decrease quickly moving away from these high P condition. These correspond to roughly $z_{rem}^L < 100$ m, meaning rather labile or light large particles, which contribute poorly to P removal and net

O production.

For $z_{rem}^L > 100$ m, LP_{org} efficiently remove P from the water column, limiting production. Coagulation rates are therefore lower and vary in a more limited range of values. For this reason, the contribution of SP_{org} to the total export below the euphotic layer is strongly dominated by the value of z_{rem}^S , with a null contribution to export for all values of $z_{rem}^S < 10$ m and increasing values above it. This trend is reflected in the deep-water small particle fraction (Figure 8c,d). Coagulation rates at depth, even though lower compared to the surface, still reach values of a few percent in the shelf sea (≤ 6 % of the exported SP_{org}). Small particles contribute up to between 5 % and 50~~75~~ % to export and up to between 5 % and 15~~50~~ % to the sediment accumulation in the shelf sea, with the highest contribution to sediment accumulation being reached for large z_{rem}^S and low z_{rem}^L . In the open ocean, small particles represent up to between 30 % and 80~~93~~ % of the total export, with the percentage being strongly dependent on the value of z_{rem}^S . Our model highlights therefore the different role of large and small particles in the determination of the equilibrium budgets and fluxes. Coagulation into large (fast sinking, less labile) particles is essential to maintain high enough sedimentation and burial rates, therefore allowing O accumulation in the system. At the same time, small (slow sinking, more labile) particles tune the total magnitude of export and remineralization below the euphotic layer, ~~impacting~~affecting the distribution of oxygen and nutrients throughout the water column.

5 Discussion

5.1 Model limitations and robustness

5.1.1 Box model limitations

BPOP consists in a simple box model with 4 ocean boxes, 2 sediment boxes and 1 atmospheric box. As with every box model, BPOP only allows a very rough and fundamental representation of the ocean's topography and circulation as well as of the exchange fluxes between ocean, atmosphere and sediments. Even though this may be a limitation in the context of the study of the well-known modern (and future) ocean, such a computationally inexpensive model can be a useful tool to for a first exploration of a large variety of projected conditions. In the context of understanding past ocean changes, often characterized by a limited availability of observational data, the use of such a simple model constitutes instead an effective and honest approach to understand global shifts in budgets and fluxes. Furthermore, BPOP explicitly distinguishes between the well sampled shelf sea and the less known open ocean of deep time, therefore allowing to relate shelf data with large scale open sea conditions.

5.1.2 Limitations connected to the biological pump representation

In our model we adopt a very simplified representation of the biological pump, including two particle classes, “small” and “large”, generated by production and coagulation, assuming that, on average, $z_{rem}^S < z_{rem}^L$. This scheme resembles the one commonly used in ocean biogeochemical models (Gruber et al., 2006; Jackson and

Burd, 2015). Our model does not include a DOM pool for reasons mostly connected to the implicit representation of the biological pump and the complete remineralization of the non-sedimented organic material at each integration step.

Modelled particles get remineralized through the water column according to their characteristic z_{rem} . Even though for simplicity we do not use a continuum spectrum of z_{rem} , the use of two particles classes is in line with observations showing two distinct peaks in the observed distribution of particles' sinking speeds (Riley et al., 2012; Alonso-González et al., 2010). Furthermore, this simplification still allows to closely approximate the empirical particle flux curve as a function of depth, also known as Martin's curve (Boyd and Trull, 2007).

We assume that z_{rem}^S and z_{rem}^L do not vary between the shelf sea and the open ocean. However, modern ocean observations show cross-shore changes in the phytoplankton community structure and sinking speeds (Barton et al., 2013). Our simplifying assumption may therefore cause the overestimation of the relative contribution of the shelf sea to the total burial flux of P_{org} . Despite this, we believe that this choice is still convenient in the context of the current model, as it allows us to reduce the number of parameters in such a simple box model representation of the ocean's biological pump.

Observations suggest that hard shelled phytoplankton types, especially calcified cells, contribute substantially to the vertical export and burial of the organic material thanks to extremely large z_{rem} despite their small size (Lam et al., 2011; Iversen and Ploug, 2010). In the present study we focus on an interval of z_{rem}^S and z_{rem}^L values that are most likely to resemble the biological pump conditions of the Neoproterozoic - early Paleozoic ocean, before the evolution of such phytoplankton types. However, the model allows to explore different ranges of z_{rem}^S and z_{rem}^L values and to tune the rate of coagulation in order to explore the influence of these phytoplankton classes.

Even though bacterial remineralization is thought to be the dominant pathway for organic matter recycling on a global scale, especially at low latitudes (Rivkin and Legendre, 2001), modern ocean coastal environments are also characterized by high grazing rates. The evolution of zooplankton and increasingly large grazers may have had a different impact on the effective z_{rem}^S and low z_{rem}^L , ~~giving due to~~ additional P_{org} transformations such as particle fragmentation due to sloppy feeding (Cavan et al., 2017; Iversen and Poulsen, 2007). These processes can limit the large particle burial rates, while resulting in the deep production of small particle, s-POM and DOM. Our model does not currently account for particle fragmentation, however the process could be easily considered in future model developments. In this context, new processes such as the sedimentation and burial of large grazers should also be considered.

5.1.3 Sensitivity to parameter choices

We discuss here the model sensitivity to changes in a set of significant parameters adopted to describe its geometry, circulation and biological processes. Overall, none of the sensitivity experiments showed significant changes in the model results and conclusions: trends in budgets and fluxes obtained varying z_{rem}^S and z_{rem}^L , as well as our main results regarding the relative deep shelf and open ocean oxygenation remain unchanged.

Among the geometrical box model parameters, a key value is represented by the percentage of shelf sea area (\mathcal{P}_{shelf}). An increase (e.g., doubling) in \mathcal{P}_{shelf} results in an overall decrease in the total budget of P and increase in O due to the larger ratio of burial to production, which is facilitated by a larger extension of the surface of shallow water. Interestingly, deep shelf anoxia is enhanced for larger \mathcal{P}_{shelf} , i.e., anoxia is observed for a wider range of

$z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ values, while the deep ocean tends to be more oxygenated. Despite a doubling of $\mathcal{P}_{\text{shelf}}$, however, model results largely remain in the same range of those found for modern $\mathcal{P}_{\text{shelf}}$.

We explored the effect of varying the physical circulation parameters. Changes in upwelling (Upw), have an important impact on the modelled ocean's budgets. An increase in Upw induces a lowering of P levels, especially in the deep shelf, due to their recirculation towards the surface and consequent uptake by production. This is coupled to an overall larger equilibrium O budget due to higher storage in the deep open ocean, and consequent recirculation into the deep shelf. Deep shelf ~~anoxia-suboxia~~ is still possible, but for a more limited range of $z_{\text{rem}}^{\text{L}}$ values. Changes in vertical mixing in the open ocean (Mix_{vo}) ~~do not seem to~~ affect the overall P and O budgets, ~~but they do impact O mostly for high $z_{\text{rem}}^{\text{L}}$~~ . For lower Mix_{vo} , the O budget decreases due to lower O storage at depth, while P increases. Changes in vertical mixing on the shelf (Mix_{vs}), instead, have a minor impact on the model's total budgets and fluxes, while locally modulating shelf oxygen and nutrient concentrations. Lateral mixing fluxes (Mix_{ls} , Mix_{ld}) were included in our model for means of generalization and in order to account for the influence of non-upwelling margins, with a lower value than in previous studies (Fennel et al., 2005). Changes in Mix_{ls} and Mix_{ld} result in significant changes in the deep ocean storage of tracers and on open ocean production, with little impact on the budget of the other ocean boxes. However, also in this case, our main conclusions remain unaffected.

We explored the impact of changing the portion of nutrients delivered directly to the open ocean, $\mathcal{P}_{\text{open}}$. Even large changes in this parameter do not significantly affect the model's results, indicating that the relative levels of P and O at equilibrium are determined by the internal physical and biogeochemical dynamics of the model, rather than by boundary conditions.

Lastly, we explored the model sensitivity to the choice of key biogeochemical parameters representing rates of transformation. Both the use of higher coagulation rates (cg_r) and the use of higher ~~higher~~ rates of formation of mineral Ca-P (CaP_r) result in a general increase in O levels and decrease in nutrient availability due to larger sedimentation and burial rates. However, we find again no substantial change in the model behaviour nor in the relative contribution to budgets and fluxes of each modelled ocean box. Furthermore, we have tested the impact of having sediment remineralization rates that vary with the particles' z_{rem} , under the assumption that the liability of small and large particles may be different. In our experiment, we increased the remineralization rm_r rate linearly with z_{rem} by 40 % of our baseline value (rm_r^0), with rm_r^0 being found at the centre of the interval of explored values of $z_{\text{rem}} = [0 \text{ m}, 450 \text{ m}]$. Under these conditions, we obtained a higher decoupling between the influence of $z_{\text{rem}}^{\text{S}}$ and $z_{\text{rem}}^{\text{L}}$ on budgets and fluxes, both being more strongly driven by the small particle properties for large values of $z_{\text{rem}}^{\text{L}}$.

5.2 Model applications

5.2.1 Past changes in the biological pump

The evolution of larger and heavier cells during the Neoproterozoic and across the Neoproterozoic-Paleozoic transition is hypothesised to have caused significant changes in the ocean's nutrient and redox state (Lenton and Daines, 2018). Our new model can be used to assess the impact of this evolution in both the shelf and the open ocean. Our first model results highlight that for small $z_{\text{rem}}^{\text{L}}$, i.e., for an early biological pump with reduced capacity of export and burial, nutrient levels and production rates are particularly high. At the same time, an increase in

z_{rem}^S alone, fuelling higher remineralization rates at depth, can induce anoxia in the deep shelf while still maintaining the deep open ocean substantially oxygenated. The possibility of a coexistence of an anoxic deep shelf with an oxygenated deep open ocean has important implications for the interpretation of deep time redox proxy data, which come almost exclusively from shelf and slope environments, yet have been widely used to infer deep ocean anoxia for most of the Proterozoic Eon (Lenton and Daines, 2017) . We plan to use our model to further explore these changes in a time-frame perspective, introducing time varying boundary conditions (such as changes in P_{in}) and parameter properties.

Phytoplankton evolution as well as the development of heavier and larger marine organisms continued throughout the Phanerozoic (Katz et al., 2007). BPOP can also be used to explore the role of the biological pump in the onset of OAEs in the course of the Mesozoic era, likely induced by enhanced productivity due to an upwelling intensification (Higgins et al., 2012). During the Mesozoic era, the evolution of dinoflagellates, calcareous and silica-encased phytoplankton also likely impacted the export and burial rates in a significant way (Katz et al., 2004). By extending the range of explored values of z_{rem}^S and z_{rem}^L , or possibly including the effect of grazing and/or an additional heavy POC class for shelled organisms, BPOP can also be used to study the consequences of such evolution.

5.2.2 Future changes in the biological pump

Predicted future changes connected to global warming include, among the others, changes in ocean temperature, pH and stratification (Gruber et al., 2004), with additional repercussions on plankton community structure, production, remineralization and export rates (Laufkötter et al., 2017; Acevedo-Trejos et al., 2014; Kwon et al., 2009). Our results show that around values of z_{rem}^L measured for modern shelf environment (Cavan et al., 2017) modelled equilibrium budgets and fluxes are very sensitive to small changes in z_{rem} . This indicates a potentially high sensitivity of the modern ocean to small changes in the biological pump, which may be particularly important in the deep shelf, where the boundary with ~~anoxia~~-suboxia is especially close (Keeling et al., 2010). Our model can be used to get a first assessment of the large-scale combined effect of predicted changes in the biological pump with expected shifts in the physical ocean properties.

5.2.3 Exploring past and future changes in geometry, physics and biogeochemistry

In the present study we have focused on the impact of changes of z_{rem}^S and z_{rem}^L on the equilibrium budget and fluxes in the ocean. However, BPOP can be used to explore the effect of global changes in other physical or biogeochemical processes coupled to the biological pump dynamics. Aside from testing the robustness of our results, the sensitivity tests presented in subsection 5.1.3 serve also as a first exploration of the possibility to apply the model to these further studies. We discuss here a few examples of past changes that could be explored with the present model.

Through Earth's history, variations in the distribution of continents and in the mean sea level height likely impacted the percentage of shelf sea area (\mathcal{P}_{shelf}) throughout the global ocean (Katz et al., 2007). Changes in climate and therefore in the mean temperature are expected to have affected both the air-sea gas exchange of oxygen (Schmidt number, $N_{Sch}(T_{mean})$) and vertical mixing (Mix_{vo}) (Petit et al., 1999). Reduced vertical mixing in warm periods is also expected to be relevant in the future because of global warming (Gruber et al., 2004). Changes in temperature are also known to impact biological activity directly, e.g., by increasing remineralization

rates (rm_r) (Laufkötter et al., 2017), and indirectly, e.g., affecting production and mortality rates through changes in the mixed layer depth (Polovina et al., 1995). ~~Lastly, e~~Climatic shifts can also cause changes in the intensity of alongshore winds and therefore in the upwelling circulation ~~(Upw)~~ (Sydeman et al., 2014). Lastly, the model can be used to test the impact of changes in the biogeochemical cycles, including shifts in the Redfield ratio as well as global changes in the P input (P_{in}) to the ocean (Reinhard et al., 2017; Filippelli, 2008).

6 Conclusions and Outlook

This paper provides a description, evaluation and discussion of the new BPOP model. BPOP is aimed at exploring the effects of changes in the biological pump on the shelf and open ocean nutrient and redox state as well as on P and O fluxes. This model can be adopted for a large variety of studies aimed at exploring the impact of changes in the biological pump, i.e., the particle remineralization length scale z_{rem} , in past and future ocean settings. Furthermore, it allows to couple changes in POM properties to changes in the ocean's geometry, circulation and boundary conditions.

Despite its simple representation of the ~~model-ocean~~ circulation and of the biological pump, the model can reasonably simulate values of the current P and O tracer budgets and biological pump fluxes. The model predicts potentially large variations in these P and O budgets and fluxes for past and future changes in the POM remineralization length. Our preliminary results also indicate that the early ocean may have been nutrient rich, with high levels of production and remineralization and that an anoxic deep shelf setting may have been compatible with an oxygenated deep open ocean.

We plan to apply this model to study the time evolution of the P and O budgets in both the shelf and the open ocean environment across the Neoproterozoic-Phanerozoic transition. Further developments of the model will be aimed at accounting for successive evolutionary innovations, including particle fragmentation due to grazing.

Code availability

- 5 The code is available for download in the supplementary material of the present publication, which also includes the user's manual.

Author contributions

- 10 TL and EL conceived the study. EL conceived and implemented the model. EL and TL evaluated and improved the model. Both authors contributed to the interpretation of the results, and to the writing of the present manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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<u>Name</u>	<u>Description</u>	<u>Units</u>
<u>P^{ss}</u>	<u>Inorganic phosphorus in surface shelf sea box</u>	<u>mmol m⁻³</u>
<u>P^{ds}</u>	<u>Inorganic phosphorus in deep shelf sea box</u>	<u>mmol m⁻³</u>
<u>P^{so}</u>	<u>Inorganic phosphorus in surface open ocean box</u>	<u>mmol m⁻³</u>
<u>P^{do}</u>	<u>Inorganic phosphorus in deep open ocean box</u>	<u>mmol m⁻³</u>
<u>O^{ss}</u>	<u>Molecular oxygen in surface shelf box</u>	<u>mmol m⁻³</u>
<u>O^{ds}</u>	<u>Molecular oxygen in deep shelf box</u>	<u>mmol m⁻³</u>
<u>O^{so}</u>	<u>Molecular oxygen in surface open ocean box</u>	<u>mmol m⁻³</u>
<u>O^{do}</u>	<u>Molecular oxygen in deep open ocean box</u>	<u>mmol m⁻³</u>
<u>O^{at}</u>	<u>Oxygen mixing ratio in atmosphere (mol mol⁻¹)</u>	<u>-</u>
<u>SedP_{org}^s</u>	<u>Organic phosphorus in the sediments of the shelf sea</u>	<u>mmol m⁻²</u>
<u>SedP_{org}^o</u>	<u>Organic phosphorus in the sediments of the open ocean</u>	<u>mmol m⁻²</u>
<u>P^{TOT}</u>	<u>Diagnostic variable: total P budget from sources and sinks only</u>	<u>Tmol P</u>
<u>O^{TOT}</u>	<u>Diagnostic variable: total O budget from sources and sinks only</u>	<u>Pmol O₂</u>

Table 1: List of the model's state variables and of their units

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Name	Description	Value	Units	Source
Mol_{atmo}	Millimoles of air in atmospheric box	$1.8 \cdot 10^{230}$	mmMoles	-
ΔZ_{eu}	Depth of the euphotic layer in shelf and open ocean	100	m	[1]

ΔZ_{ds}	Depth of the deep shelf sea box	100	m	[2]
ΔZ_{do}	Depth of the deep open ocean box	3500	m	[3]
A_{ocean}	Total area covered by the ocean	$361 \cdot 10^{12}$	m ²	-
\mathcal{P}_{shelf}	Fraction of the total ocean area currently covered by the shelf sea (≤ 200 m deep)	0.07	-	Barrón and Duarte (2015)

Table 42: Parameters set that describes the box model's geometry: [1] we assume a constant average euphotic layer depth of 100 m in both shelf and open sea; [2] the shelf sea is assumed to be 200 m deep in total, in line with the definition of shelf sea by Barrón and Duarte (2015); [3] we assume an average open ocean depth of 3600 m (including euphotic layer).

Name	Description	Value	Units	Source
P_{ini}	Initial P concentration for all the ocean boxes	2.2	mmol m ⁻³	Watson et al. (2017)
O_{ini}	Initial O concentration for all the ocean & atmosphere boxes	0	mmol m ⁻³	-
$(P_{org})_{ini}$	Initial P_{org} in all the sediment boxes	0	mmol m ⁻³	-
Upw	Upwelling cell mass fluxes	5.5	Sv	Chavez and Messié (2009)
Mix_{vo}	Vertical mixing in the open ocean	40	Sv	[1]
Mix_{ls}	Lateral mixing at the surface	0 4.5	Sv	[2]
Mix_{ld}	Lateral mixing at depth	0 4.5	Sv	[2]
Mix_{vs}	Vertical mixing in the shelf sea	0.5 1	Sv	[3]
<u>spv</u>	<u>Seconds per year conversion factor (Sv to m³ yr⁻¹)</u>	<u>31557600</u>	<u>s yr⁻¹</u>	<u>-</u>
P_{in}	Total P river input	0.092 · <u>10^{12}</u>	10^{12} Tmmol yr ⁻¹	Slomp and Van Cappellen (2006)
\mathcal{P}_{open}	Fraction of river input delivered to the open ocean	0.4	-	[4]
OP_{Red}	Oxygen to phosphorus Redfield ratio	106 150	-	Anderson and Sarmiento (1994) [5]
T_{mean}	Global mean temperature for oxygen's Schmidt number	17.64	°C	Sarmiento and Gruber (2006)
W_{speed}	Global mean wind speed for oxygen gas transfer velocity	7.5	m/s	Sarmiento and Gruber (2006)
T_{mean}	Global mean temperature for oxygen gas transfer velocity	17.64	°C	Sarmiento and Gruber (2006)
K_{Henri}	Henry's law constant	$770 \cdot 10^{-6}$	m ³ atm mmol ⁻¹	-
$Omix_0$	Today's oxygen mixing ratio in atmosphere	0.21	-	-

W_0	Baseline oxidative weathering flux coefficient	$9.752 \cdot 10^{15}$	$\frac{\text{mmol}}{\text{Mmol}} \frac{\text{Mmol}}{\text{yr}^{-1}}$	[56]

Table 32: Parameters set pertaining to the model's initial conditions, circulation mass fluxes, boundary fluxes. Notes: [1] compare to: 38 Sv (Sarmiento and Gruber, 2006), 17 Sv of mixing flux in the Southern Ocean alone (Meyer et al., 2015), estimated open ocean downwelling 38.5 Sv and upwelling 34.5 Sv (Ganachaud and Wunsch, 2000); [2] cross-shelf mass exchange due to lateral recirculation, tides and mixing aimed at including exchange processes other than upwelling (Fennel et al., 2005; Cole et al., 2015; Wollast, 1998); [3] minimal assumption for vertical mixing in nearshore regions due to seasonal and eddy mixing, see also subsection 3.2 Sensitivity to parameter choices; [4] up to 70% of river outflow reaches the open ocean, see Sharples et al. (2017); [5] assuming a constant 1:1 = C:O₂ ratio and a Redfield ratio of C:P=106; [56] calculated from the equilibrium solution given P_{in}.

Name	Description	Value	Units	Source
P_{eff}	P maximum uptake <u>rate for production efficiency</u>	0.8	yr^{-1}	[1]
K_P	Michaelis Menten constant for P uptake	0.2	mmol m^{-3}	[2]
K^{so}_O	Michaelis Menten constant for aerobic remineralization <u>in the sediments</u>	0.2	mmol m^{-3}	[3]
K^{wo}_O	<u>Michaelis Menten constant for aerobic remineralization in the watercolumn</u>	15	mmol m^{-3}	[4]
c_{gr}	Coagulation rate of small Porg into large Porg	0. 36 18	$\frac{(\text{mmol m}^{-3})^{-1}}{\text{yr}^{-1}}$	[54]
r_{mr}	Remineralization rate of sedimented Porg	0. 73 36	yr^{-1}	[64]
f_{ean}	<u>Remineralization enhancement factor under anoxia</u>	1.25	=	Slomp and Van Cappellen (2006)
CaPr	Rate of formation of Ca-P mineral from sedimented Porg	0. 40 .2	$\frac{(\text{mmol m}^{-2})^{-1}}{\text{yr}^{-1}}$	[75]
f_{san}	<u>Ca-P formation dampening factor under anoxia</u>	0.5	=	Slomp and Van Cappellen (2006)

Table 43: Parameters set pertaining to the model's Porg cycle and coupled biogeochemical fluxes: [1] maximum P uptake rate, meant to account for environmental limitations of phytoplankton growth rate (such as light and temperature), the magnitude of the rate keeps into account that we are not explicitly resolving phytoplankton concentrations (order of $10^{-2} \text{ mmolP m}^{-3}$), see also production in Gruber et al. (2006) and Yool & Tyrrell (2003); [2] measured values vary in the range of 0.01 mmol m^{-3} up to a few mmol m^{-3} , varying for different phytoplankton types, see Lomas et al. (2014), Tantanararit et al. (2013), Krumhardt et al. (2013), Lin et al. (2016), Klausmeier et al. (2004); [3] biogeochemical models commonly switch to anaerobic respiration below 4 mmol m^{-3} (Paulmier et al., 2009), measured half-saturation constant for oxygen uptake varies in the range of $0.1 - 3 \text{ mmol m}^{-3}$ (Ploug, 2001); [4] biogeochemical models commonly switch to anaerobic respiration below 4 mmol m^{-3} (Paulmier et al., 2009), measurements suggest a value close to 19 mmol m^{-3} (DeVries and Weber, 2017); [5] on the same order of magnitude as Gruber et al. (2006); [6] one order of magnitude smaller than Gruber et al. (2006) to allow more surface recycling in absence of an explicitly resolved P_{org} pool; [75] unmeasured – given the analogous adopted functional form, we assume Ca-P formation to happen on a timescale close to that of P_{org} coagulation in the water column.

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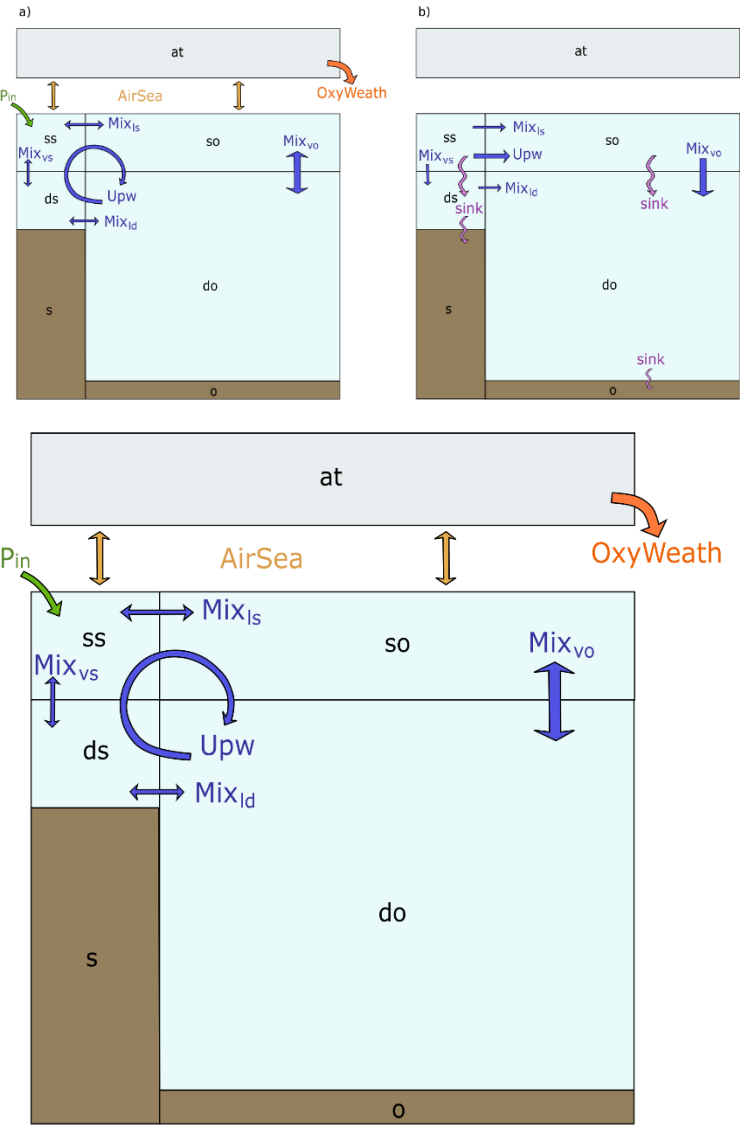
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<u>Quantity</u>	<u>Model</u>	<u>Modern values or estimates</u>	<u>Units</u>	<u>Source</u>
<u>Total ocean P</u>	<u>2500 - 2800</u>	<u>3100</u>	<u>TmolP</u>	Watson et al. (2017)
<u>Total ocean O₂</u>	<u>100 - 140</u>	<u>225-310</u>	<u>PmolO₂</u>	Duursma and Boisson (1994); Keeling et al. (1993)
<u>P^{ss}</u>	<u>1.5 - 1.9</u>	<u>1 - 1.5</u>	<u>mmol m⁻³</u>	Garcia et al. (2018b); Sarmiento and Gruber (2006)
<u>P^{ds}</u>	<u>3.9 - 5.4</u>	<u>2.2</u>	<u>mmol m⁻³</u>	Garcia et al. (2018b); Watson et al. (2017)
<u>P^{so}</u>	<u>0.4 - 1.1</u>	<u>0.2 - 2</u>	<u>mmol m⁻³</u>	Garcia et al. (2018b); Sarmiento and Gruber (2006)
<u>P^{do}</u>	<u>2.0 - 2.3</u>	<u>1 - 3</u>	<u>mmol m⁻³</u>	Garcia et al. (2018b); Sarmiento and Gruber (2006)
<u>O^{ss}</u>	<u>273 - 274</u>	<u>200 - 350</u>	<u>mmol m⁻³</u>	Garcia et al. (2018a)
<u>O^{ds}</u>	<u>2.8 - 12.3</u>	<u>0 - 80</u>	<u>mmol m⁻³</u>	Garcia et al. (2018a)
<u>O^{so}</u>	<u>273</u>	<u>200 - 350</u>	<u>mmol m⁻³</u>	Garcia et al. (2018a)
<u>O^{do}</u>	<u>72 - 110</u>	<u>40 - 200</u>	<u>mmol m⁻³</u>	Garcia et al. (2018a)
<u>Production (Prod)</u>	<u>18.8 - 51.5</u>	<u>35 - 80</u>	<u>GtC yr⁻¹</u>	Carr et al. (2006)
<u>Export</u>	<u>2.8 - 4.0</u>	<u>4 - 20</u>	<u>GtC yr⁻¹</u>	Henson et al. (2011)
<u>Export production</u>	<u>8 % - 30 %</u>	<u>2 % - 20 %</u>	<u>of total Prod</u>	Boyd and Trull (2007)

Burial	<u>0.3 % - 0.8 %</u>	<u>0.4 %</u>	<u>of total Prod</u>	Sarmiento and Gruber (2006)
Shelf sea production	<u>12 % - 25 %</u>	<u>20 %</u>	<u>of total Prod</u>	Barrón and Duarte (2015); Wollast (1998)
Shelf sea export	<u>21 % - 27 %</u>	<u>29 %</u>	<u>of total Export</u>	Sarmiento and Gruber (2006)
Shelf sea burial	<u>100 %</u>	<u>91 %</u>	<u>of total Burial</u>	Sarmiento and Gruber (2006)

Table 5: Summary of the model evaluation provided in section 3. Modern observations and estimates are compared to model results obtained for z_{rem}^L in the range of measured values for a modern shelf sea (Cavan et al., 2017).

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Figure 1: Box model scheme with a representation of: **a)** the physical and boundary fluxes affecting inorganic tracers the state variables in the water column and atmosphere, where blue arrows indicate advective and mixing fluxes and yellow arrows indicate air/sea gas exchange fluxes; **b)** physical fluxes affecting the implicitly modelled P_{org} variable, where straight blue arrows indicate advective and mixing fluxes while bent pink arrows indicate gravitational sinking fluxes. The model includes 7 boxes: surface shelf (ss), deep shelf (ds), surface open ocean (so), deep open ocean (do), atmosphere (at), shelf sediments (s), open ocean sediments (o).

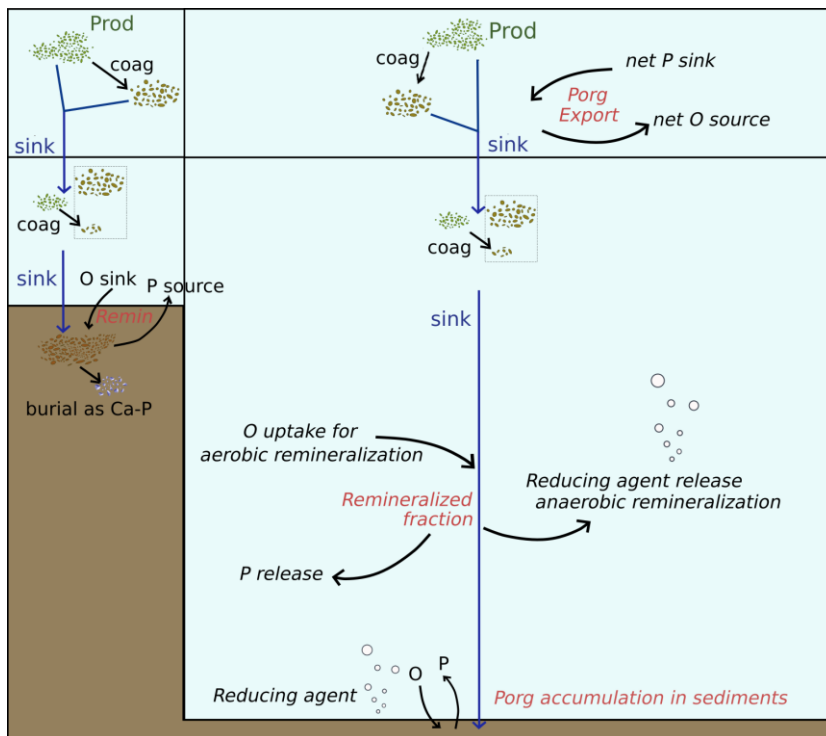
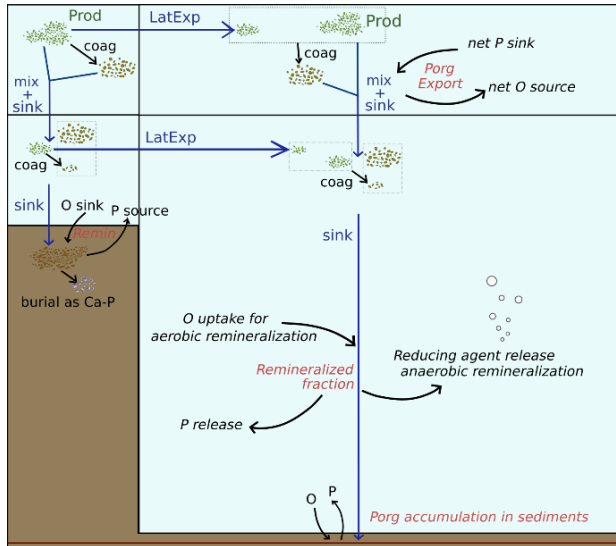


Figure 2: Representation of the physical and biogeochemical fluxes affecting the P_{org} cycling in the model. Even though some processes (such as burial as Ca-P) are here represented in detail only in one box, the set of biogeochemical processes regulating the P_{org} dynamics in shelf sea and open ocean (both water column and sediments) is the same, as described in subsection 2.2.

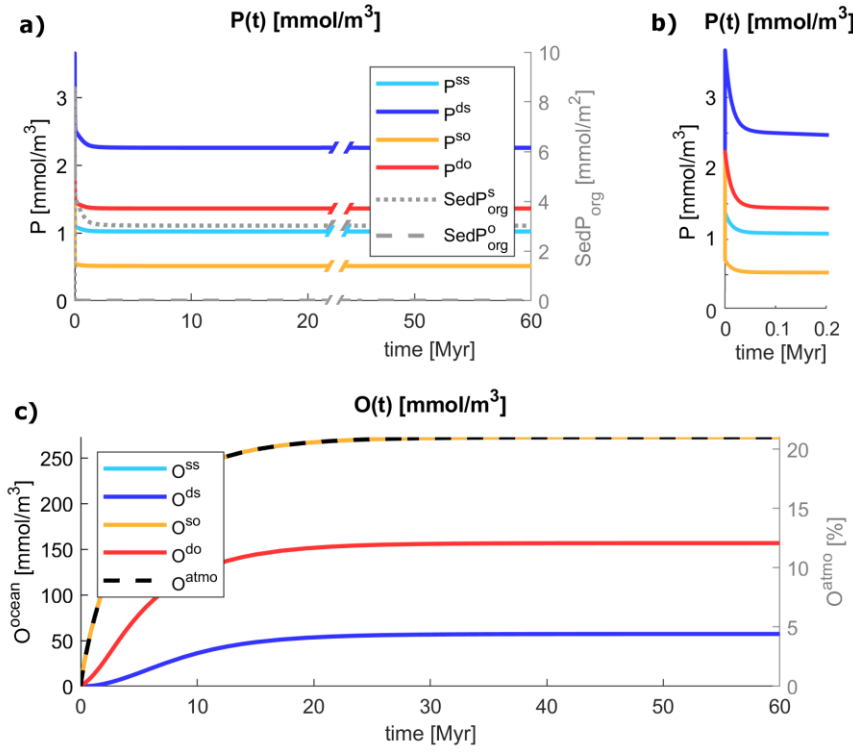


Figure 3: Evolution of the state variables from the initial conditions listed in Table 2 and remineralization lengths roughly in the middle of the interval of explored values: $z_{rem}^S = 20$ m, $z_{rem}^L = 250$ m. (a) Evolution of inorganic phosphorus P in the water column (left axis) and of organic phosphorus in the sediments $SedP_{org}$ (right axis); (b) zoom on the dynamics of P in the first two hundred thousand years; (c) Evolution of oxygen in the water column (left axis) and atmosphere (right axis). In subplot (c) the two lines O^{ss} and O^{so} are overlapping: the two variables evolve closely due to the coupling of the surface ocean with the atmosphere via air-sea gas exchange.

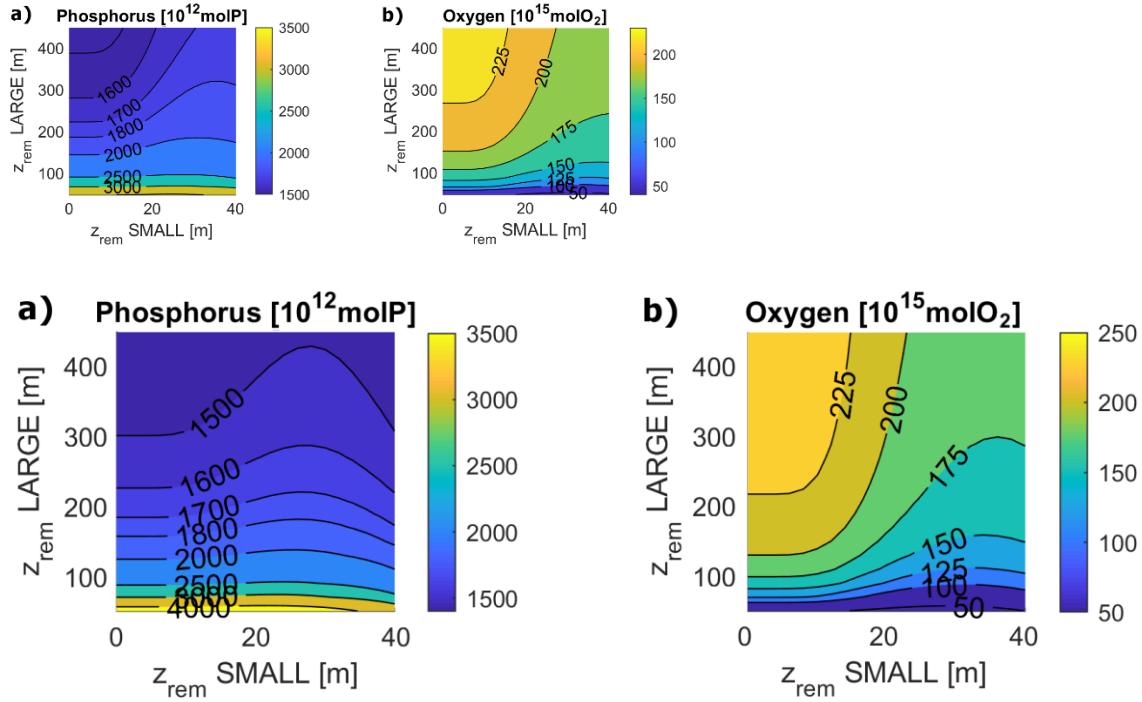


Figure 43: Total ocean budgets of (a) P and (b) O at equilibrium for varying z_{rem}^S and z_{rem}^L .

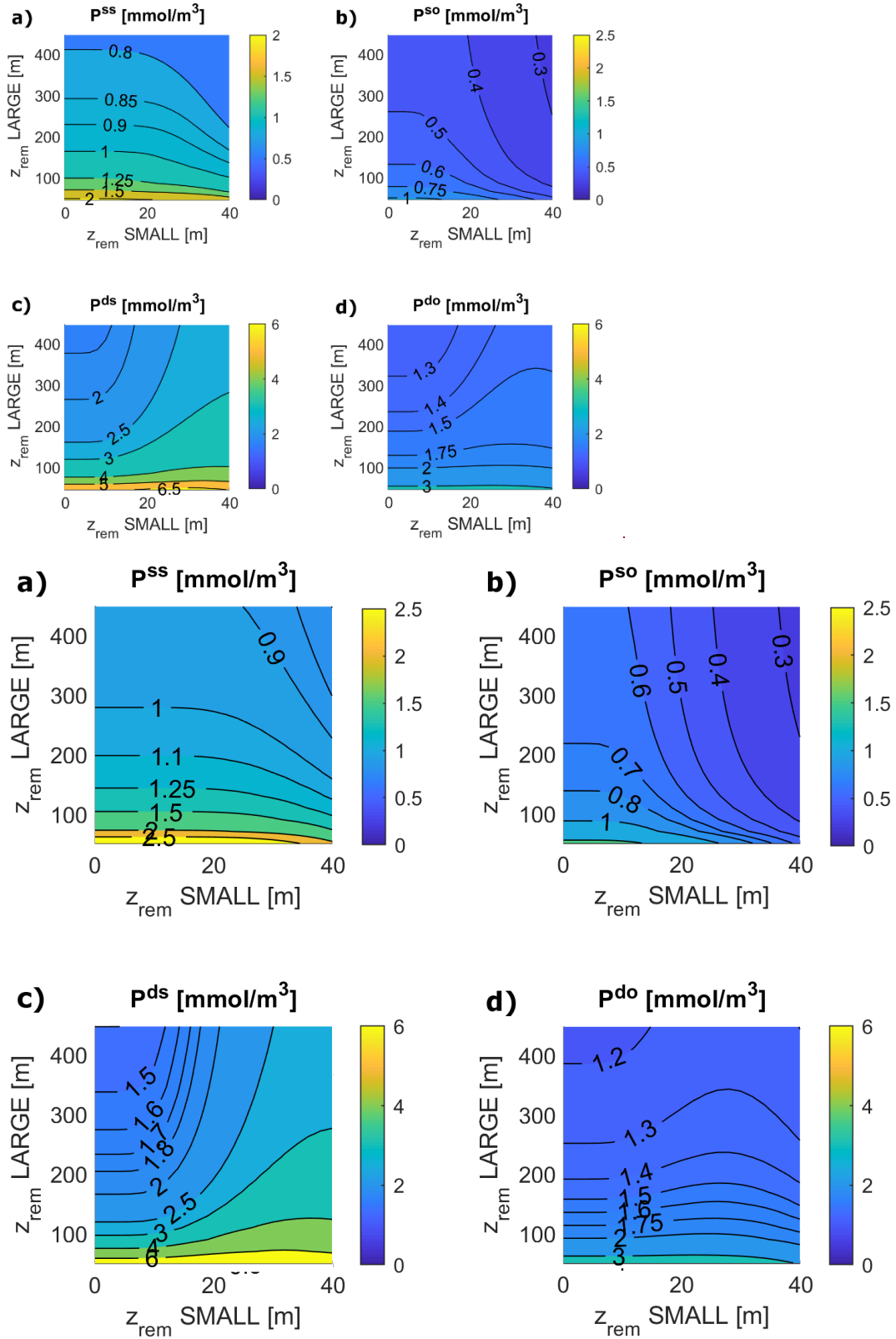


Figure 54: Local P concentration in each ocean box for varying z_{rem}^S and z_{rem}^L : (a) surface shelf sea, ss; (b) surface open ocean, so; (c) deep shelf sea, ds; (d) deep open ocean, do. Surface ocean boxes, as well as deep ocean boxes, are plotted on the same scale.

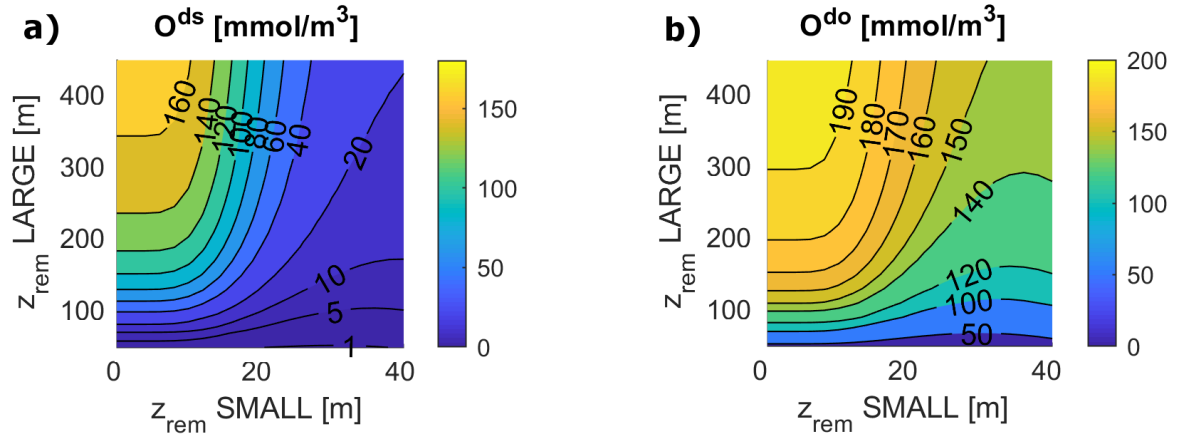
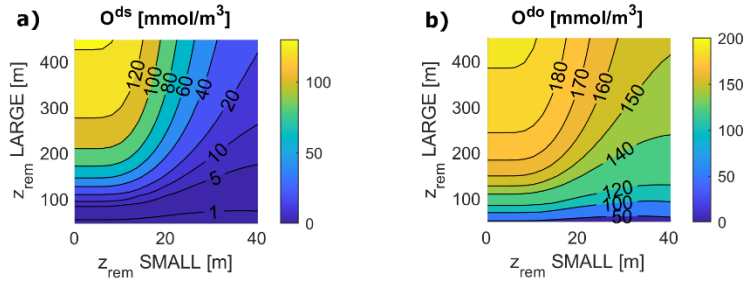


Figure 65: O concentrations at equilibrium for varying z_{rem}^S and z_{rem}^L : (a) deep shelf sea, ds; (b) deep open ocean, do. Surface ocean boxes (not shown) have nearly constant values of O for any set of z_{rem} due to the air-sea gas exchange, which strongly couples them to the atmosphere.

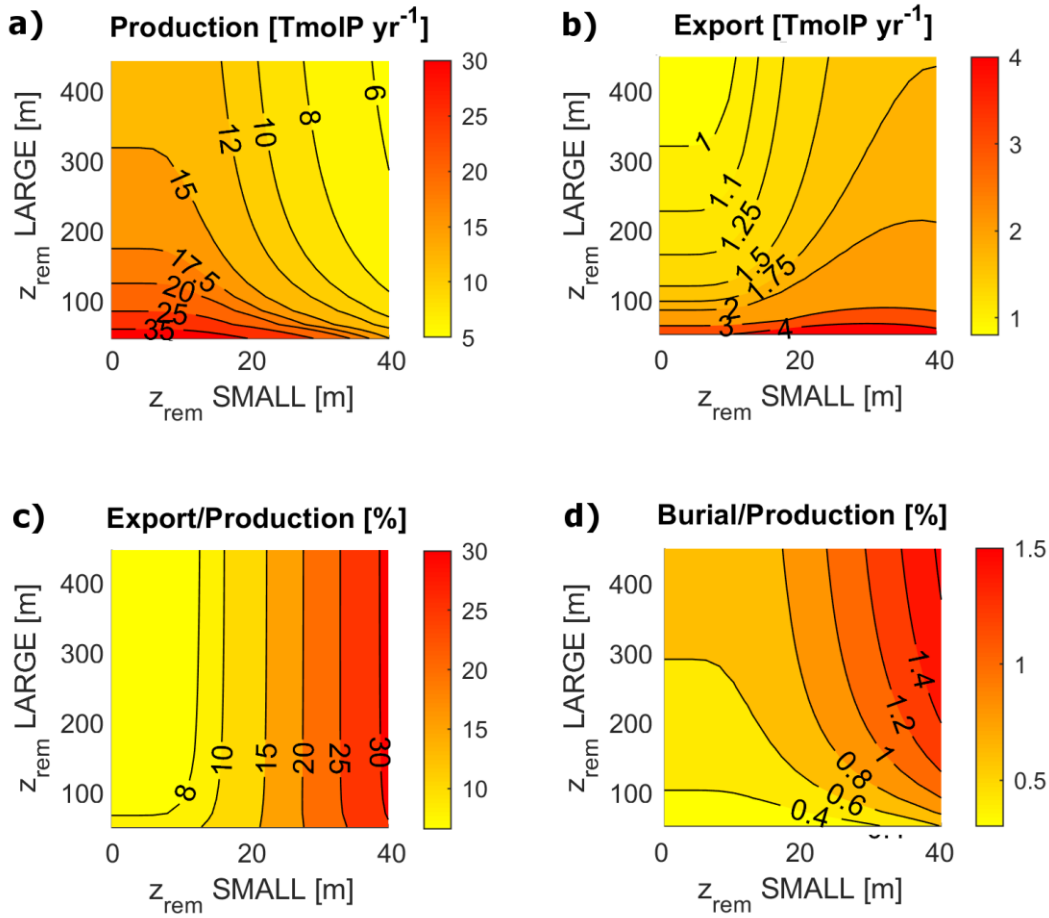
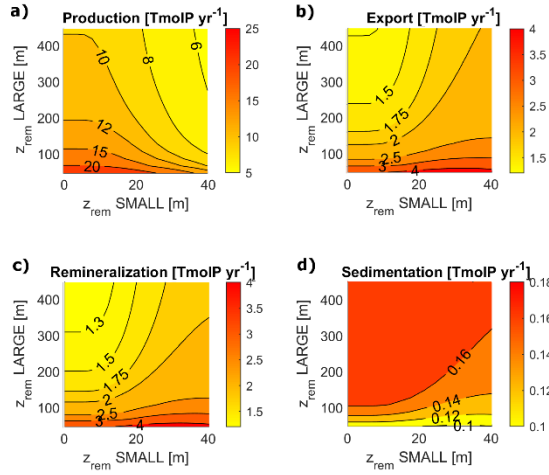


Figure 76: Biological pump fluxes in P units for the entire ocean for varying z_{rem}^S and z_{rem}^L : (a) P_{org} surface production; (b) P_{org} export through the euphotic layer depth; (c) ~~P_{org} deep remineralization in both water column and sediments~~; Export production, i.e. export to production ratio (d)- ~~Burial to production ratio~~ P_{org} sedimentation at the ocean bottom.

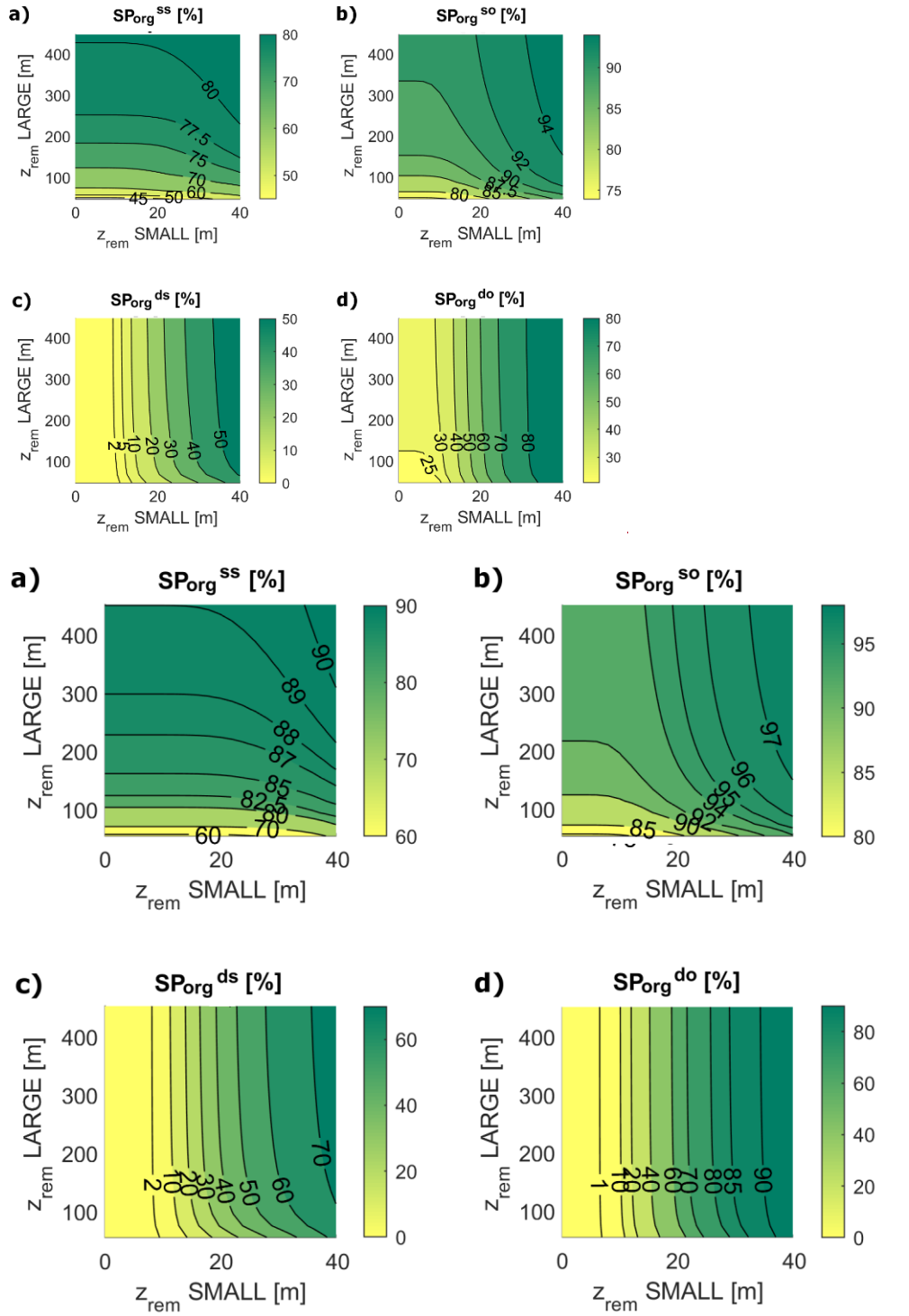


Figure 87: Small P_{org} (SP_{org}) fraction after coagulation in the surface and at depth for varying z_{rem}^S and z_{rem}^L : (a) surface shelf sea, ss; (b) surface open ocean, so; (c) deep shelf sea, ds; (d) deep open ocean, do.

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Appendix A: Equations

A.1 Air-sea gas exchange of oxygen

$$15 \quad N_{Sch} = 1638 - 81.83 \cdot T_{mean} + 1.483 \cdot T_{mean}^2 - 0.008004 \cdot T_{mean}^3 \quad (A1)$$

$$K_W = 0.31 \cdot W_{speed}^2 \cdot \sqrt{660/N_{Sch}} \cdot 10^{-2} \cdot (24 \cdot 365.25); \quad (A2)$$

20

A.2 Surface shelf sea (ss)

$$V^{ss} = \Delta Z_{eu} \cdot A_{ocean} \cdot \mathcal{P}_{shelf} \quad (A3)$$

$$Prod^{ss} = P_{eff} \cdot (P^{ss} / (P^{ss} + K_p)) \cdot P^{ss} \quad (A4)$$

$$SP_{org}^{ss} = Prod^{ss} - cg_r \cdot (Prod^{ss})^2 \quad (A5)$$

$$25 \quad LP_{org}^{ss} = cg_r \cdot (Prod^{ss})^2 \quad (A6)$$

$$\text{LatExp}^{ss} = SP_{org}^{ss} \cdot (Upw + Mix_{ls}) / V^{ss} \quad (A7)$$

$$VExp_{SP_{org}}^{ss} = (SP_{org}^{ss} - \text{LatExp}^{ss}) \cdot (\exp(-(\Delta Z_{eu}/2) / z_{rem}^S) + Mix_{vs} / V^{ss}) \quad (A78)$$

$$30 \quad VExp_{LP_{org}}^{ss} = LP_{org}^{ss} \cdot (\exp(-(\Delta Z_{eu}/2) / z_{rem}^L) + Mix_{vs} / V^{ss}) \quad (A89)$$

$$\frac{dP^{ss}}{dt} = P_{in} \cdot (1 - \mathcal{P}_{open}) / V^{ss} + (Upw \cdot (P^{ds} - P^{ss}) + Mix_{ls} \cdot (P^{so} - P^{ss}) + Mix_{vs} \cdot (P^{ds} - P^{ss})) \cdot spy / V^{ss} \\ - (VExp_{SP_{org}}^{ss} + VExp_{LP_{org}}^{ss})$$

$$(A94)$$

$$AirSea^{ss} = K_W \cdot (O^{at}/K_{Henri} - O^{ss}) \cdot (A_{ocean} \cdot \mathcal{P}_{shelf})/V^{ss} \quad (A104)$$

$$OProd^{ss} = OP_{Red} \cdot (VExp_{SP_{org}}^{ss} + VExp_{LP_{org}}^{ss}) \quad (A112)$$

$$5 \quad \frac{dO^{ss}}{dt} = (Upw \cdot (O^{ds} - O^{ss}) + Mix_{ls} \cdot (O^{so} - O^{ss}) + Mix_{vs} \cdot (O^{ds} - O^{ss})) \cdot spy/V^{ss} + AirSea^{ss} \\ + OProd^{ss} \quad (A123)$$

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A.3 Deep shelf sea (ds)

$$V^{ds} = \Delta Z_{ds} \cdot A_{ocean} \cdot \mathcal{P}_{shelf} \quad (A134)$$

$$15 \quad VInp_{SP_{org}}^{ds} = VExp_{SP_{org}}^{ss} \cdot (V^{ss}/V^{ds}) \quad (A145)$$

$$SP_{org}^{ds} = VInp_{SP_{org}}^{ds} - cg_r \cdot (VInp_{SP_{org}}^{ds})^2 \quad (A156)$$

$$20 \quad LP_{org}^{ds} = VExp_{LP_{org}}^{ss} \cdot (V^{ss}/V^{ds}) + cg_r \cdot (VInp_{SP_{org}}^{ds})^2 \quad (A167)$$

$$\cancel{LatExp^{ds} = SP_{org}^{ds} \cdot Mix_{ld}/V^{ds}} \quad (A18)$$

$$Rem_{SP_{org}}^{ds} = \cancel{(SP_{org}^{ds} - LatExp^{ds})} \cdot (1 - \exp(-\Delta Z_{ds}/z_{rem}^S)) \quad (A179)$$

$$Rem_{LP_{org}}^{ds} = LP_{org}^{ds} \cdot (1 - \exp(-\Delta Z_{ds}/z_{rem}^L)) \quad (A1820)$$

$$25 \quad AerRem_{SedP_{org}}^{ds} = rm_r \cdot SedP_{org}^s / \Delta Z_{ds} \cdot (O^{ds} / (O^{ds} + K_O^S K_{\theta})) \quad (A1924)$$

$$AnaRem_{SedP_{org}}^{ds} = (rm_r \cdot fe_{an}) \cdot SedP_{org}^s / \Delta Z_{ds} \cdot (1 - O^{ds} / (O^{ds} + K_O^S)) \quad (A20)$$

$$\frac{dP^{ds}}{dt} = (Upw \cdot (P^{do} - P^{ds}) + Mix_{ld} \cdot (P^{do} - P^{ds}) + Mix_{vs} \cdot (P^{ss} - P^{ds})) \cdot spy/V^{ds} \\ ++ (Rem_{SP_{org}}^{ds} + Rem_{LP_{org}}^{ds} + AerRem_{SedP_{org}}^{ds} + AnaRem_{SedP_{org}}^{ds})$$

$$\text{---} + (Rem_SP_{org}^{ds} + Rem_LP_{org}^{ds} + Rem_SedP_{org}^{ds})$$

(A212)

$$AerRemWcO^{ds} = OP_{Red} \cdot (Rem_SP_{org}^{ds} + Rem_LP_{org}^{ds}) \cdot (O^{ds} / (O^{ds} + K_O^w K_O^g))$$

5 (A223)

$$AerSedRemSedO^{ds} = OP_{Red} \cdot AerRem_SedP_{org}^{ds} \quad (A234)$$

$$\frac{dO^{ds}}{dt} = (Upw \cdot (O^{do} - O^{ds}) + Mix_{ld} \cdot (O^{do} - O^{ds}) + Mix_{vs} \cdot (O^{ss} - O^{ds})) \cdot spy / V^{ds} - AerRemWcO^{ds} - AerSedRemSedO^{ds}$$

10 (A245)

A.4 Surface open ocean (so)

$$V^{so} = \Delta Z_{eu} \cdot A_{ocean} \cdot (1 - \mathcal{P}_{shelf})$$

15 (A26A25)

$$Prod^{so} = P_{eff} \cdot (P^{so} / (P^{so} + K_P)) \cdot P^{so}$$

(A267)

$$LatInp^{so} = SP_{org}^{ss} \cdot (Upw + Mix_{ls}) / V^{so} \quad (A28)$$

$$SP_{org}^{so} = (Prod^{so} + LatInp^{so}) - cgr \cdot ((Prod^{so}) + LatInp^{so})^2$$

20 (A2729)

$$LP_{org}^{so} = cgr \cdot (Prod^{so} + LatInp^{so})^2$$

(A2830)

$$VExp_SP_{org}^{so} = SP_{org}^{so} \cdot (\exp(-(\Delta Z_{eu}/2) / z_{rem}^S) + Mix_{vo} / V^{so})$$

(A2931)

$$VExp_LP_{org}^{so} = LP_{org}^{so} \cdot (\exp(-(\Delta Z_{eu}/2) / z_{rem}^L) + Mix_{vo} / V^{so})$$

25 (A302)

$$\frac{dP^{so}}{dt} = P_{in} \cdot \mathcal{P}_{open} / V^{ss} + (Upw \cdot (P^{ss} - P^{so}) + Mix_{ls} \cdot (P^{ss} - P^{so}) + Mix_{vo} \cdot (P^{do} - P^{so})) \cdot spy / V^{so} - (VExp_SP_{org}^{so} + VExp_LP_{org}^{so}) +$$

$$\text{---} (VExp_SP_{org}^{so} + VExp_LP_{org}^{so})$$

30 (A313)

$$AirSea^{so} = K_W \cdot (O^{at}/K_{Henri} - O^{so}) \cdot (A_{ocean} \cdot (1 - \mathcal{P}_{shelf}))/V^{so}$$

(A324)

$$OProd^{so} = OP_{Red} \cdot (VExp_{SP_{org}}^{so} + VExp_{LP_{org}}^{so})$$

(A335)

$$5 \quad \frac{dO^{so}}{dt} = (Upw \cdot (O^{ss} - O^{so}) + Mix_{ls} \cdot (O^{ss} - O^{so}) + Mix_{vo} \cdot (O^{do} - O^{so})) \cdot spy/V^{so} + AirSea^{so} + OProd^{so}$$

(A346)

A.5 Deep open ocean (do)

$$10 \quad V^{do} = \Delta Z_{do} \cdot A_{ocean} \cdot (1 - \mathcal{P}_{shelf})$$

(A357)

$$VInp_{SP_{org}}^{do} = VExp_{SP_{org}}^{so} \cdot (V^{so}/V^{do})$$

(A368)

$$\text{LatInp}^{do} = SP_{org}^{ds} \cdot Mix_{ld}/V^{do} \quad (A39)$$

$$15 \quad SP_{org}^{do} = (VInp_{SP_{org}}^{do} + \text{LatInp}^{do}) - cg_r \cdot (VInp_{SP_{org}}^{do} + \text{LatInp}^{do})^2$$

(A3740)

$$LP_{org}^{do} = VExp_{LP_{org}}^{so} \cdot (V^{so}/V^{do}) + cg_r \cdot (VInp_{SP_{org}}^{do} + \text{LatInp}^{do})^2$$

(A3841)

$$Rem_{SP_{org}}^{do} = SP_{org}^{do} \cdot (1 - \exp(-\Delta Z_{do}/Z_{rem}^S)) \quad (A3942)$$

$$20 \quad Rem_{LP_{org}}^{do} = LP_{org}^{do} \cdot (1 - \exp(-\Delta Z_{do}/Z_{rem}^L)) \quad (A403)$$

$$AerRem_{SedP_{org}}^{do} = rm_r \cdot SedP_{org}^o/\Delta Z_{do} \cdot (O^{do}/(O^{do} + K_O^S K_{\sigma}))$$

(A414)

$$AnaRem_{SedP_{org}}^{do} = (rm_r \cdot fe_{an}) \cdot SedP_{org}^o/\Delta Z_{do} \cdot (1 - O^{do}/(O^{do} + K_O^S)) \quad (A42)$$

$$\frac{dP^{do}}{dt} = (Upw \cdot (P^{so} - P^{do}) + Mix_{ld} \cdot (P^{ds} - P^{do}) + Mix_{vo} \cdot (P^{so} - P^{do})) \cdot spy/V^{do}$$

$$25 \quad + (Rem_{SP_{org}}^{do} + Rem_{LP_{org}}^{do} + AerRem_{SedP_{org}}^{do} + AnaRem_{SedP_{org}}^{do}) +$$

$$+ (Rem_{SP_{org}}^{do} + Rem_{LP_{org}}^{do} + Rem_{SedP_{org}}^{do})$$

(A435)

$$AerRemWcO^{do} = OP_{Red} \cdot (Rem_{SP_{org}}^{do} + Rem_{LP_{org}}^{do}) \cdot (O^{do}/(O^{do} + K_O^W K_{\sigma}))$$

30 (A446)

$$AerSedRemSedO^{do} = OP_{Red} \cdot AerRemSedP_{org}^{do} \quad (A457)$$

$$\frac{dO^{do}}{dt} = (Upw \cdot (O^{so} - O^{do}) + Mix_{ld} \cdot (O^{ds} - O^{do}) + Mix_{vo} \cdot (O^{so} - O^{do})) \cdot spy/V^{do} - AerRemWcO^{do} - AerSedRemSedO^{do}$$

5 (A4648)

A.6 Shelf sea sediments (s)

$$SedFlx^s = (SP_{org}^{ds} - LatExp^{ds}) \cdot \exp(-\Delta Z_{ds}/z_{rem}^s) + LP_{org}^{ds} \cdot \exp(-\Delta Z_{ds}/z_{rem}^L) \cdot \Delta Z_{ds} \quad (A4749)$$

$$CaPform^s = CaP_r \cdot (SedP_{org}^s)^2 \cdot (O^{ds}/(O^{ds} + K_O^w) + f_{san} \cdot (1 - O^{ds}/(O^{ds} + K_O^w))) \quad (A4850)$$

$$RemSedP_{org}^{ds} = AerRemSedP_{org}^{ds} + AnaRemSedP_{org}^{ds} \quad (A49)$$

$$\frac{dSedP_{org}^s}{dt} = SedimFlx^s - CaPform^s - RemSedP_{org}^{ds} \cdot \Delta Z_{ds}$$

15 (A5054)

A.7 Open ocean sediments (o)

$$SedFlx^o = (SP_{org}^{do} - LatExp^{do}) \cdot \exp(-\Delta Z_{do}/z_{rem}^s) + LP_{org}^{do} \cdot \exp(-\Delta Z_{do}/z_{rem}^L) \cdot \Delta Z_{do} \quad (A512)$$

$$CaPform^o = CaP_r \cdot (SedP_{org}^o)^2 \cdot (O^{do}/(O^{do} + K_O^w) + f_{san} \cdot (1 - O^{do}/(O^{do} + K_O^w))) \quad (A523)$$

$$RemSedP_{org}^{do} = AerRemSedP_{org}^{do} + AnaRemSedP_{org}^{do} \quad (A53)$$

$$\frac{dSedP_{org}^o}{dt} = SedimFlx^o - CaPform^o - RemSedP_{org}^{do} \cdot \Delta Z_{do}$$

25 (A544)

A.8 Atmosphere (at)

$$AirSea^{at} = (AirSea^{ss} + AirSea^{so})/(Mol_{atmo} \cdot 10^3) \quad (A555)$$

$$AnaRemWc^{ds} = OP_{Red} \cdot (Rem_{SP_{org}}^{ds} + Rem_{LP_{org}}^{ds}) \cdot (1 - O^{ds} / (O^{ds} + K_O^w K_{\theta}))$$

(A5656)

$$AnaRemWc^{do} = OP_{Red} \cdot (Rem_{SP_{org}}^{do} + Rem_{LP_{org}}^{do}) \cdot (1 - O^{do} / (O^{do} + K_O^w K_{\theta}))$$

(A5757)

$$5 \quad AnaRemWc^{at} = (AnaRemWc^{ds} \cdot V^{ds} + AnaRemWc^{do} \cdot V^{do}) / (Mol_{atmo} \cdot 10^3)$$

(A5858)

$$AnaRemSed^{at} = (AnaRem_{SedP_{org}}^{ds} \cdot V^{ds} + AnaRem_{SedP_{org}}^{do} \cdot V^{do}) / Mol_{atmo} \quad (A59)$$

$$OxyWeath = W_0 \cdot \sqrt{O^{at} / Omix_0} / (Mol_{atmo} \cdot 10^3) \quad (A6059)$$

$$\frac{dO^{at}}{dt} = -AirSea^{at} - AnaRemWc^{at} - OxyWeath$$

(A619)

A.9 Diagnostics: Total budgets of P and O

$$P_{sources} = P_{in} \cdot 10^{-15} \quad (A62)$$

$$25 \quad P_{sinks} = (CaPform^s \cdot A_{ocean} \cdot \mathcal{P}_{shelf} + CaPform^o \cdot A_{ocean} \cdot (1 - \mathcal{P}_{shelf})) \cdot 10^{-15} \quad (A63)$$

$$\frac{dP^{TOT}}{dt} = P_{sources} - P_{sinks} \quad (A64)$$

$$30 \quad O_{sources} = (OProd^{ss} \cdot V^{ss} + OProd^{so} \cdot V^{so}) \cdot 10^{-18} \quad (A65)$$

$$O_{sinks} = ((SedRemO^{ds} + AerRem^{ds}) \cdot V^{ds} + (SedRemO^{do} + AerRem^{do}) \cdot V^{do} + OxyWeath \cdot Mol_{atmo}) \cdot 10^{-18} \quad (A66)$$

$$35 \quad \frac{dO^{TOT}}{dt} = O_{sources} - O_{sinks}$$

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