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

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Abstract

Previous studies have suggested that enhanced weathering and benthic phosphorus (P) fluxes, triggered by climate warming, can increase the oceanic P inventory on millennial time scales, promoting ocean productivity and deoxygenation. In this study, we assessed the major uncertainties in projected P inventories and their imprint on ocean deoxygenation using an Earth system model of intermediate complexity for a business-as-usual carbon dioxide (CO_2) emission scenario until the year 2300 and subsequent linear decline to zero emissions until the year 3000 and hence without significant differences in climate and circulation.

Model results suggest a large spread in the simulated oceanic P inventory due to uncertainties in (1) assumptions for weathering parameters, (2) the representation of bathymetry on slopes and shelves in the model bathymetry, (3) the parametrization of benthic P fluxes and (4) the representation of sediment P inventories. Our best estimate for changes in the global ocean P inventory by the year 5000 caused by global warming amounts to +30% compared to pre-industrial levels. Weathering, benthic and anthropogenic fluxes of P contributed +25%, +3% and +2% respectively. The total range of oceanic P inventory changes across all model simulations varied between +2% and +60%. Suboxic volumes were up to 5 times larger than in a model simulation with a constant oceanic P inventory. Considerably large amounts of the additional P left the ocean surface unused by phytoplankton via physical transport processes as preformed P. In the model, nitrogen fixation was not able to adjust the oceanic nitrogen inventory to the increasing P levels or to compensate for the nitrogen loss due to increased denitrification. This is because low temperatures and iron limitation inhibited the uptake of the extra P and growth by nitrogen fixers in polar and lower latitude regions. We suggest that uncertainties in P weathering, nitrogen fixation and benthic P feedbacks need to be reduced to achieve more reliable projections of oceanic deoxygenation on millennial timescales.

1 Introduction

Many different processes affect the oxygen balance in the ocean (e.g. oxygen solubility, stratification, respiration, circulation, Levin, 2019; Oschlies et al., 2018). Oceanic phosphorus (P) inventories are known to substantially affect oceanic oxygen inventories on millennial timescales (Tsandev and Slomp, 2009; Palastanga et al., 2011; Monteiro et al., 2012). Phosphorus is considered the ultimate limiting

nutrient for ocean productivity at the global scale (Tyrrell, 1999). Elevated supply of P to the ocean stimulates production and export of organic matter and deoxygenation, which possibly drives more intense oxygen depletion in the oxygen deficient zones and along the continental margins, with release of additional P from sediments turning anoxic (Van Cappellen and Ingall, 1994; Palastanga et al.,

40   2011). Such a positive feedback was discussed for a global warming scenario under present-day conditions (Niemeyer et al., 2017) as well as for large-scale deoxygenation events in the Cretaceous era, the so-called oceanic anoxic events (OAEs) (Tsandev and Slomp, 2009; Monteiro et al., 2012; Ruvalcaba Baroni et al., 2014). For the Cretaceous, it has been suggested that atmospheric carbon dioxide (CO_2) concentrations as high as 1000 to 3000 ppmv, driven by enhanced CO_2 outgassing from

45   volcanic activity (Jones and Jenkyns, 2001; Kidder and Worsley, 2012), have triggered OAEs (Damsté et al., 2008; Méhay et al., 2009; Bauer et al., 2016). The warmer climate during past OAEs increased weathering on land (Blättler et al., 2011; Pogge von Strandmann et al., 2013), leading to an enhanced supply of nutrients, in particular P, increasing the oceanic nutrient inventory and driving the positive feedback mentioned above. Furthermore, the enhanced release of P from sediments were suggested to

50   maintain high levels of productivity in the Cretaceous ocean (Mort et al. 2007; Kraal et al. 2010), which would contribute to the development of OAEs. Evidence in the palaeo record indicates that the Earth has experienced several OAEs with large-scale anoxia, euxinia and mass extinctions (Kidder and Worsley, 2010).

Could such OAEs also appear in the near future under contemporary global warming? High CO_2

55   concentrations in the atmosphere seem to be one driver for initiating OAEs and ocean deoxygenation. Projected anthropogenic CO_2 emissions may lead to atmospheric CO_2 concentrations exceeding 1000 ppmv at the beginning of the 22nd century if emissions continue to increase in a business-as-usual scenario (Meinshausen et al., 2011). Although anthropogenic CO_2 emissions occur over a short period compared to the long-term and relatively constant volcanic CO_2 emissions during OAEs (Kidder and

60   Worsley, 2012), elevated atmospheric CO_2 concentrations will persist for many millennia (Clark et al., 2016). This may provide the conditions for long-term climate change and large-scale deoxygenation. There is thus some concern that anthropogenic CO_2 emissions could potentially trigger another OAE (Watson et al., 2017). Yet, Kidder and Worsley (2012) argue that emissions of global fossil fuel reserves are insufficient to drive a modern OAE, but may instead lead to widespread suboxia.

65   During climate warming, ocean productivity could switch from P to nitrogen (N) limitation (Saltzman, 2005). N limitation could arise from enhanced denitrification in a more anoxic ocean, but at the same time low N to P ratios would be expected to stimulate N_2-fixation by diazotrophs (Kuypers et al., 2004). N_2-fixation in regional proximity with OMZs can lead to net N losses due to mass balance constraints (Landolfi et al., 2013), which may even reverse the net effect of N_2-fixation on the nitrogen

70   inventory.

Recently, Niemeyer et al. (2017) showed in a model study that P weathering and sedimentary P release in a business-as-usual CO_2-emission (RCP8.5) scenario could strongly enlarge the marine P inventory and lead to a 4 to 5-fold increase in the suboxic water volume (dissolved oxygen (O_2) concentrations less than 5 mmol m^{-3}) on millennial timescales. Here, we build on this study and test the sensitivity of

75   the marine P and O_2 inventories in a climate change scenario on millennial timescales to different

model formulations of P weathering and benthic fluxes. We aim to provide better constraints on future ocean deoxygenation and assess the biogeochemical feedbacks triggered by P addition. In Sect. 2 we present the experimental design and the model parameterizations of continental P weathering and of benthic P release. In Sect. 3 we assess uncertainties in P fluxes due to different assumptions about the P weathering fluxes, different model formulations of benthic P burial and improved representation of bathymetry and anthropogenic P fluxes. Consequences for deoxygenation and for the biogeochemical cycling of nutrients are discussed.

2 Model and Experimental Design

2.1 Model

We applied the University of Victoria (UVic) Earth System Model (ESM) version 2.9 (Weaver et al., 2001), which has been used in several studies to investigate ocean oxygen dynamics (Schmittner et al., 2007; Oschlies et al., 2008; Getzlaff et al., 2016; Keller et al., 2016; Landolfi et al., 2017). The UVic model consists of a terrestrial model based on TRIFFID and MOSES (Meissner et al., 2003), an atmospheric energy-moisture-balance model (Fanning and Weaver, 1996), a sea-ice model (Bitz and Lipscomb, 1999) and the general ocean circulation model MOM2 (Pacanowski, 1996). Horizontal resolution of all model components is 1.8° latitude x 3.6° longitude. The ocean model has 19 layers with layer thicknesses ranging from 50 m for the surface layer to 500 m in the deep ocean. The marine ecosystem was represented by a NPZD model (Keller et al., 2012). Organic matter transformations (production, grazing, degradation) were parameterized using fixed stoichiometric molar ratios (C:N:P, 106:16:1) and directly related to the production and, in oxygenated waters, utilization of O_2 (O:P, 160). When O_2 is depleted in the model, organic matter is respired using nitrate (NO_3^-) (i.e. microbial denitrification). An O_2 concentration of 5 mmol m^{-3} was used as the switching point from aerobic respiration to denitrification. Sedimentary denitrification was not considered in this model configuration so that water column denitrification and N_2-fixation dictate the oceanic N balance. No explicit iron cycle was simulated and iron limitation was approximated with prescribed seasonally varying dissolved iron concentrations (Keller et al., 2012). Parameterizations of benthic and weathering fluxes of P were extended from the study of Niemeyer et al. (2017). Implementations of a calcium carbonate sediment model (Archer, 1996) and a parameterization for silicate and carbonate weathering (Meissner et al., 2012) were applied in all simulations. When P weathering and anthropogenic P fluxes were applied (see Sect. 2.2), the global P flux was distributed over all river basins, in every grid box, weighted by river discharge rates.

2.2 Experimental Design

Twelve different model simulations were performed to explore the range of uncertainties for the long-term development of the oceanic P inventory (Table 1). Each simulation started from an Earth system state close to equilibrium under preindustrial atmospheric CO_2 concentrations, prescribed wind fields and present-day orbital forcing. Spin-up runs lasting 20,000 simulation years or longer were made for each simulation to reach equilibrium. In the spin-up runs for simulations with benthic P burial (purple

and red in Table 1), the marine P inventory was kept constant by instantaneously compensating oceanic P loss (burial) by P weathering fluxes to the ocean. For model simulations without benthic P burial (black and blue in Table 1), one common spin-up run was performed without P weathering fluxes.

All transient simulations started in the year 1765 and ended in the year 5000. Simulations were forced with anthropogenic CO_2 emissions (fossil fuel and land use change) according to the extended RCP 8.5 scenario until the year 2300 (Meinshausen et al., 2011), followed by a linear decline to zero CO_2 emissions by the year 3000. Warming from non-CO_2 greenhouse gases and the effect of sulphate aerosols were prescribed as radiative forcing (Eby et al., 2013). Non CO_2-emission effects from land-use change were not considered. The reference simulation (*Ref*) was performed without weathering and without burial fluxes of P, meaning that the P inventory of the ocean remained unchanged. The remaining transient simulations applied either variable climate-sensitive weathering anomalies (without burial) or time-variable burial fluxes (with constant weathering) to the ocean (Table 1).

2.3 Burial experiments

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

Fractional coverage of every ocean grid box by seafloor was calculated on each model depth level according to the subgrid bathymetry (Somes et al., 2013). The subgrid bathymetry was inferred from ETOPO2v2[1] (National Geophysical Data Center, 2006). ETOPO2v2 has a horizontal resolution of 2-minutes fine enough to adequately represent continental shelves and slopes. The coarse standard model bathymetry in the UVic model has a horizontal resolution of 1.8° latitude x 3.6° longitude.

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

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

where RR_P is the detritus flux from the ocean (in P units). BEN_P was calculated locally by a "transfer function", which parameterizes sediment/water exchange of P as a function of the rain rate of organic matter and the bottom water O_2 concentration. Preferential P release, relative to carbon (C), is observed in sediments overlain by O_2-depleted bottom waters (Ingall and Jahnke, 1994). Benthic P release was dependent on the dissolved inorganic carbon release (BEN_C) from organic matter degradation in the sediment and the C:P regeneration ratio $r_{C:P}$ (Wallmann, 2010; equation 2):

$$BEN_P = \frac{BEN_C}{r_{C:P}}. \tag{2}$$

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[1] https://www.ngdc.noaa.gov/mgg/global/etopo2.html

BEN_C was computed (Eq. 3a) as the difference of the carbon rain rate to the sediment (RR_C) and a 'virtual' organic carbon burial flux (BUR_C). Virtual is meant in the sense that there is no explicit burial of organic C in the model, and instead all organic C is remineralized in the deepest ocean layer. In this study we do not focus on changes in the C inventory and therefor BUR_C is just calculated to determine BEN_C in Eq. (2). BUR_C is dependent on the simulated organic C rain rate and bathymetry (Flögel et al., 2011). Burial of organic C is more efficient on the shelf and continental margins (Eq. 3b) than for the deep sea (Eq. 3c, sediment below 1000m water depth):

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

$$BUR_C = 0.14 \cdot RR_C^{1.11}, \tag{3b}$$

$$BUR_C = 0.014 \cdot RR_C^{1.05}, \tag{3c}$$

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

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

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

Burial fluxes of P were applied in the simulations *Bur, Bur_Dun, Bur_low, Bur_high, Bur_noSG* and *Bur_res*. The default *Bur* model configuration uses Eq. (3) (Flögel et al., 2011) and the subgrid-scale bathymetry. Uncertainties in benthic P burial were examined by modifying this default model configuration.

In the *Bur_Dun* (i.e. burial parameterization from Dunne et al. 2007) simulation BUR_C was calculated using Eq. (5) with RR_C in mmol C m^{-2} d^{-1}; Dunne et al. (2007):

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

Where c = 7 mmol C m^{-2} d^{-1}. This parameterization leads to high (low) organic C burial rates for high (low) organic C rain rates. This formulation is different to the standard formulation of burial in Eq. (3b, c) where burial depends on the C rain rates and in addition on the water depth. In the standard formulation, C burial is by definition one magnitude larger in slope and shelf regions compared to the deep ocean (see Eq. 3b, c).

We examined the sensitivity of P burial to the uncertainty of the parameters in Eq. (4) describing the carbon to phosphorus regeneration ratio $r_{C:P}$. Given means and standard deviations for the parameters Y_F=123±24; A=112±24; r=32±19 and assuming a Gaussian distribution, 100,000 independent coefficient combinations were assembled to calculate offline a range of global P burial estimates. For the offline calculation, preindustrial fields of O_2 and RR_C were extracted from the simulation *Bur* with a temporal resolution fine enough to resolve seasonal variations in the data. Global P burial varied between 0.21 TmolP a^{-1} (*Bur_low*) and 0.60 TmolP a^{-1} (*Bur_high)* for a confidence interval of 90% (coefficients are shown in Table 1). Individual spin-ups were performed for the *Bur_low* and *Bur_high* simulation to check that the offline calculated P burial corresponded to the online values from the spin-up. Only minor differences between the O_2 fields of the *Bur* spin-up and the spin-ups for *Bur_low* and

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

For the simulation *Bur_noSG* (i.e. without subgrid-scale parameterization), P fluxes at the sediment-ocean interface were calculated using the coarser standard model bathymetry, which barely reproduce the global coverage of shelf areas (compare hypsometries in suppl. Fig. S1). This does not affect other processes like circulation, advection or mixing.

The implemented transfer functions (Eq. 2 and 4) assume unlimited local reservoirs of sedimentary P, meaning that the cumulative release of P may exceed the local inventory of P in the sediment if the benthic release is sustained over a longer period of time. In the simulation *Bur_res* (i.e. restricted release or P reservoir) we tested the impact of this simplification by applying sediment inventory restrictions to sediment P release. In accordance to Flögel et al. (2011), release of P from the deeper ocean (>1000 m) cannot exceed the rain rate of organic P to the sediment. For the continental shelf and slope, an upper limit sediment P inventory was calculated based on the following assumptions. We assume that the top 10 cm of the sediment column are mixed by organisms and are hence regarded as the active surface layer that is in contact with the overlying bottom water. Considering a mean porosity of 0.8 and a mean density of dry particles of 2.5 g cm^{-3}, the mass of solids in this layer is 5 g cm^{-2} (Burwicz et al., 2011). The mean concentration of total P in continental shelf and slope sediments is 0.07 wt-% equal to 22.6 µmol/g (Baturin, 2007). Together, these assumptions convert to a maximum local inventory of total solid P in the active surface layer of $RES_{P,max}$ = 113 µmol cm^{-2} (Eq. 6a). We assume that shelf and slope sediments can release up to 100 % of the total solid P under low oxygen conditions. The local P inventory (RES_P) can be fully replenished by P supply from the water column and any excess P is assumed to be permanently buried:

$$\{RES_P \in \mathbb{R} \mid 0 \geq RES_P \geq RES_{P,max}\} \tag{6a}$$

$$\frac{\Delta RES_P}{\Delta t} = RR_P - BEN_P \tag{6b}$$

Local values of RES_P adjust during the spin-up according to the environmental conditions. Our pragmatic sediment inventory approach most likely overestimates the upper limit of P that can be released from the sediments. For example, under low O$_2$ conditions, part of the releasable or reactive P is transformed into authigenic P and permanently buried (Filippelli, 2001).

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

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

2.4 Weathering Experiments

Uncertainties in the ocean P inventory due to weathering processes and anthropogenic fluxes of P were examined with the model simulations *Anthr, Weath0.05, Weath0.10, Weath0.15* and *Weath0.38*.

In simulations *Weath0.05, Weath0.10, Weath0.15, Weath0.38* (i.e. the number represents the preindustrial weathering flux) the global weathering flux of P to the ocean (W_P) was parameterized in terms of an anomaly relative to a preindustrial P weathering flux ($W_{P,0}$) according to Eq. (8).

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

The weathering function f is given in Eq. (9). Values of $W_{P,0}$ are given in Table 1 and derived below. The chosen anomaly approach assumes that, at steady state, $W_{P,0}$ is balanced by a respective global burial flux and hence can be neglected during the spin-up. In these simulations no benthic P burial was applied and for preindustrial conditions the weathering function f(NPP,SAT) equals 1 and hence W_P equals 0 TmolP a^{-1}. The dynamic weathering function f (Eq. 9) was adopted from Niemeyer et al. (2017) and is originally based on an equation from Lenton and Britton (2006) for carbonate and silicate weathering. Following Niemeyer et al. (2017), we assumed that the release of P is proportional to the chemical weathering of silicates and carbonates on a global scale. Equation (9) describes the sensitivity of terrestrial weathering to the change of global terrestrial net primary production (*NPP*) and global mean surface air temperature (*SAT*):

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

with NPP_0 and SAT_0 being the respective preindustrial values. Increasing *SAT* and *NPP* lead to enhanced weathering. The upper estimate of $W_{P,0}$ in *Weath0.38* was inferred from the P burial reference simulation *Bur*, assuming that the global integral of burial is compensated by the preindustrial global weathering flux (i.e. the global marine P inventory is in steady state). With the simulations *Weath0.05*, *Weath0.10*, *Weath0.15*, *Weath0.38* we explored the range of $W_{P,0}$ estimates as derived from observational studies, which range from 0.05 to 0.30 TmolP a^{-1} (see Fig. 1, Benitez-Nelson, 2000; Compton et al., 2000; Ruttenberg, 2003). These studies give a range of total P fluxes to the oceans, which are higher than interfered from dissolved inorganic P fluxes shown already in previous studies (e.g. Martin and Meybeck, 1979; Rao and Berner, 1993) and in the Global News Model (Seitzinger et al., 2005). A small amount of fluvial P is delivered to the ocean as dissolved inorganic P, but the majority (90%) is particulate (inorganic and organic) P (Compton et al., 2000). The fast transformations between dissolved and particulate P in rivers (seconds to hours) (Withers and Jarvie, 2008) suggest a much higher amount of P that is available for marine organism than derived from dissolved inorganic P concentrations. A large amount of bioavailable P in rivers is present as loosely sorbed and iron-bound P. Estimates of bioavailable P are given in Fig. 1 (Benitez-Nelson, 2000; Compton et al., 2000; Ruttenberg, 2003), which are much higher than the estimates for dissolved inorganic P (0.018 TmolP a^{-1} from Seitzinger et al. (2005) or 0.03 TmolP a^{-1} from Filippelli (2002)). Taking into account only fluxes of dissolved inorganic P would strongly underestimate the effect of weathering fluxes as a P source to the ocean. The weathering parametrization (Eq. 9) was used to scale preindustrial fluvial fluxes of bioavailable P that is delivered in UVic to the ocean as dissolved inorganic P. In the model, no distinction was made between particular and dissolved fluvial fluxes of P. Uncertainties to other weathering parameterizations were not investigated in this study. Our parameterization predicts similar weathering rates to other weathering formulations (Meissner et al., 2012, their Fig. 6a). Since weathering is calculated on a global scale, we cannot study the effects of regional lithology and soil shielding on weathered P (Hartmann et al., 2014). UVic neither resolves the P cycle in the rivers, which is an active field for scientific research (Beusen et al., 2016; Harrison et al., 2019).

Finally, global anthropogenic P fluxes from fertilization, soil loss due to deforestation and sewage as projected by Filippelli (2008) were prescribed in the simulation *Anthr* (anthropogenic).

3. Uncertainties in Phosphorus Inventory

The large range of projected global phosphorus (P) fluxes to the ocean from sediments or weathering (Fig. 2a) leads to uncertainties in future P inventories by up to 60% of the present-day value until the year 5000 (Fig. 2b). All simulations show negligible differences in atmospheric CO_2 concentrations and hence undergo a similar climate development. Maximum CO_2 concentrations of 2200 ppmv were reached in the year 2250 and then declined to 1100 ppmv by the year 5000, comparable to results from Clark et al. (2016).

3.1. Fluvial P Fluxes: Weathering and Anthropogenic

Largest uncertainties in the P inventory are related to the large range of P weathering fluxes (Fig. 2, blue curves). Upper and lower estimates of P weathering fluxes differ by a factor of 6 (Fig. 2a, blue lines). In our weathering simulations, weathering anomalies depend linearly on the preindustrial weathering flux, $W_{P,0}$, estimate (see Eq. 8) because the climate development is essentially equal across the simulations. Therefore, the choice of $W_{P,0}$ (Fig. 1a) is a major source of uncertainty for projected future land-ocean P fluxes.

Weathering fluxes increased from the pre-industrial value by a factor of 2.5 until the year 5000 for atmospheric CO_2 concentrations of 1100 ppmv. This is comparable with the two- to four–fold increase in weathering fluxes estimated during OAE 2 approximately 91 Ma ago (Pogge von Strandmann et al., 2013) when atmospheric CO_2 concentrations increased to about 1000 ppmv (Damsté et al., 2008).

In contrast to weathering-induced P input, anthropogenic P fluxes (Filippelli, 2008) influence the global marine P inventory only in the near future (Fig. 2a, black dashed line). A decline in anthropogenic P fluxes after the year 2100 is expected due to the depletion of the easily reachable phosphorite mining reserves (Filippelli, 2008).

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

The release of P from the sediment is strongly dependent on the O_2 concentration in the water above the sediments (Wallmann 2003; Flögel et al. 2011). Climate warming reduces O_2 solubility and ventilation of the ocean, which decreases the global O_2 content (more details in Sect. 4). The general decrease in ocean O_2 content may therefore cause preferential release of P from marine sediments. Differences in sediment P fluxes in our simulations are related to uncertainties in the parameterization of the transfer function (Fig. 2, red lines, -0.01 to 0.22 TmolP a^{-1} by the year 5000), to different representations of the bathymetry (Fig. 2, purple dashed line, 0.06 (without subgrid) and 0.12 (*Bur*) TmolP a^{-1}) and to the way sediment P reservoirs in the sediment are represented (Fig. 2, purple solid line, -0.01 (limited reservoir) and 0.12 (unlimited reservoir, *Bur*) TmolP a^{-1}).

The global P burial of approximately 0.2 TmolP a^{-1} (Fig. 3) (Filippelli and Delaney, 1996; Benitez-Nelson, 2000; Ruttenberg, 2003) is relatively well reproduced by simulations *Bur_low* and *Bur_Dun*. The simulation with the standard UVic bathymetry (*Bur_noSG*) underestimates P burial by 60% while the simulations *Bur_high*, *Bur* and *Bur_res* overestimate P burial by 180%, 90% and 80% with respect to estimates based on observations. The transient response of the P release to O_2 was stronger for simulations with low burial and vice versa (Fig. 2), except for simulation *Bur_res*. In *Bur_res*, a

significant reduction in the transient P release occurred due to the implementation of a finite P reservoir, with net global P loss due to enhanced burial at the end of the simulation. In the year 5000, global P concentrations increased in *Bur_res* by only 0.06 mmolP m^{-3} compared to the global mean pre-industrial concentration of 2.17 mmolP m^{-3}. This is six-fold smaller than the increase of 0.36 mmolP m^{-3} in simulation *Bur* with an assumed unlimited P reservoir. The small increase in the oceanic P inventory in *Bur_res* can be explained by the reduction in P sediment inventory rather than by changes in the rain rate of particulate organic matter to the sediment (RR_C). In *Bur*, a rapid increase in the benthic P release appeared in areas where the water turned suboxic and thus drove a positive benthic feedback between P release, productivity and deoxygenation. A limited supply of P from the sediment (*Bur_Res*) dampens this feedback.

Simulated pre-industrial RR_C increased significantly from 180 to 1040 TgC a^{-1} on the shelf and globally from 900 to 1500 TgC a^{-1} compared to simulations without subgrid bathymetry. Pre-industrial RR_C with subgrid bathymetry agrees better to estimates by Bohlen et al. (2012) (Table 2) and to other field data studies reporting a range from 900 to 2300 TgC a^{-1} (Fig. 4) (Muller-Karger et al., 2005; Burdige, 2007; Dunne et al., 2007; Bohlen et al., 2012).

In summary, subgrid bathymetry leads to a substantial improvement of the representation of RR_C to the sediment. More realistic benthic fluxes of P could be also attained by adjusting parameters for $r_{C:P}$ (Eq. 4) or by using the function of Dunne et al. (2007) to calculate BUR_C (Eq. 5). The implementation of a finite P reservoir in the sediment has a substantial impact on the transient development of the global P inventory on millennial time scales.

4. Ocean Deoxygenation and Suboxia

Climate change influences ocean oxygen content by changes in circulation, ocean temperature and the degradation of organic matter. In warming surface waters, the solubility of O$_2$ decreases along with an increase in stratification, which together cause the deeper ocean to becomes less ventilated (Bopp et al., 2002; Matear and Hirst, 2003; Oschlies et al., 2018; Shaffer et al., 2009). Changes in export production and the degradation of organic matter in the ocean interior also affects O$_2$ content. In the following, we analyze the impact of different ocean P inventories on ocean deoxygenation and suboxia (Fig. 5). For a more detailed analysis we compare *Weath0.15* to the *Ref* simulation. In the *Weath0.15* simulation, the assumed preindustrial weathering flux compares well to estimates from observations (Fig. 1).

In the *Ref* simulation, global suboxic volume increased due to climate change from 0.3 to 1% until the year 5000 and the suboxic sediment area increased from 0.06 to 0.23% (Fig. 5, black line). In the *Weath0.15* simulation, the increase in suboxic volume (suboxic sediment area) was more than 2 (3) times higher than for the *Ref* simulation. The expansion of suboxic sediment areas was also enhanced for simulations with benthic fluxes, which could be related to regional feedbacks between increasing marine productivity, decreasing oxygen and enhanced sedimentary P release (Tsandev and Slomp, 2009). The explicitly simulated finite sedimentary P reservoir in simulation *Bur_res* places an upper limit to the benthic release of P and dampens these regional feedbacks, resulting in a weaker spreading of suboxic waters by only 17% compared to the *Ref* simulation.

330   In the following sections, we show how the expansion of suboxia is related to net primary production in the ocean (NPP), the export of organic matter (Sect. 4.1) and to nitrogen limitation (Sect. 4.2). Finally, we show how changes in O_2 solubility and utilization vary over time and affect the global O_2 inventory (Sect. 4.3). The latter approach gives another perspective because changes in O_2 inventories are a global integrated signal in comparison to the extent of suboxia, which are a consequence of more

335   local processes.

4.1. Enhanced Biological Pump

The biological carbon pump can be summarized as the supply of biologically sequestered CO_2 to the deep ocean. In the euphotic zone phytoplankton and diazotrophs take up CO_2, a process that is intensified by elevated PO_4 concentrations in the surface ocean (Fig. 6a). Part of the organic matter

340   sinks out of the euphotic zone (Fig. 6b) to the ocean interior, where it is respired using O_2. It is therefore P supply to the surface waters that explains the differences in deoxygenation between the simulations. Circulation changes could also affect the supply of O_2 to the ocean interior. However, no significant differences in climate and circulation appeared among the simulations and therefore the global-warming induced circulation changes affected all simulations in the same way.

345   In the *Ref* simulation, net primary production (NPP, Fig. 6a black line) increased from 45 to 70 TmolP a^{-1} (57 to 89 GtC a^{-1}) by the end of the simulation. In *Weath0.15*, enhanced P supply to the ocean led to a doubling of NPP compared to the *Ref* simulation. The P inventory increased continuously, but NPP did not follow this trend and instead peaked in the year 4000. In the year 5000, all simulations, excluding *Weath0.38*, showed a similar response of NPP to the P addition with an increase in NPP of

350   19 TmolP a^{-1} (relative to the *Ref* simulation) per 10% increase in P inventory. In *Weath0.38* the response was weaker and NPP increased by 8 TmolP a^{-1} per 10% rise in the P concentration. P is less effectively utilized in simulations with large oceanic P inventories. Higher ocean temperatures enhanced remineralization of organic matter in the shallower ocean so that the overall export to NPP ratio decreased from its preindustrial value of 0.12 to an average value among all simulations of 0.08

355   by the year 5000. To summarize, NPP and export of organic matter is sensitive to P addition. However, the proposed positive feedback between P, NPP, export of organic matter, and deoxygenation was limited in our simulations due to a negative feedback related to nitrate availability. This is shown and explored in the following section.

4.2. Nitrogen Limitation

360   At the end of the spin-up the N sink by denitrification and the N source by N_2-fixation were balanced. In the *Ref* simulation, climate warming enlarged the oxygen minimum zones, which enhanced denitrification in the tropics (not shown). In our model, diazotrophs are limited by P and Fe and are not limited by N. Their growth rate, which depends on temperature being zero below 15ºC, is slower relative to non-fixing phytoplankton. These characteristics allow them to succeed in warm, low-N and

365   high–P environments that receive sufficient iron. In all simulations, N_2-fixation was stimulated by the addition of P to the ocean and was sensitive to rapid changes in the supply of P (compare Fig. 7a and Fig. 2a). However, N_2-fixers (Fig. 7a) were not able to use the extra P supply in polar and iron limited

regions where low temperatures and iron limitation, respectively inhibit their growth (Fig. 8). This lead to a substantial amount of excess phosphate in the surface waters of these regions (Fig. S2). Because N2 fixers were not able to balance the loss by denitrification, nitrate decreased globally by 4 mmolN m$^-$^{3} until the year 5000 (Fig. 7b). The loss in nitrate led to a decrease in globally averaged N to P ratios. In the *Ref* simulation, N:P decreased from 14 to 12 and for the *Weath0.15* simulation it decreased to 10, which contributed further to a N limiting ocean. The nitrogen cycle was not able to recover from the decrease in N:P ratio with respect to pre-industrial values. We acknowledge that in the current study we did not account for potential future changes in iron concentrations (from atmospheric deposition, shelf inputs) and that the lack of a fully prognostic iron model may lead to a different sensitivity of the response of diazotrophs. Similarly we did not account for the ability of phytoplankton to adapt to changing N:P ratios, that may affect marine biological productivity and in turn deoxygenation. These would require further studies.

4.3. Temporal Variations of Deoxygenation

Anomalies in circulation, ocean temperature and remineralisation of organic matter affect oceanic O_2 levels in a climate-warming scenario. In the *Ref* simulation, the O_2 inventory (Fig. 9a) decreased by 60 Pmol O_2 by the year 3000 and then reached present day values again by the year 5000. In *Weath0.15*, weathered P enhanced deoxygenation and led to a greater decrease in O_2 than in the *Ref* simulation. The O_2 decrease was up to 70 Pmol in the year 3300 and O_2 still showed a negative anomaly of 24 Pmol O_2 by the year 5000. Global anomalies in oxygen were due to changes of the Apparent Oxygen Utilization (AOU, Fig. 9b) and the O_2 saturation level (Fig. 9c). AOU is calculated from the difference between the O_2 saturation concentration and the in situ oxygen concentration assuming that all ocean water leave the surface layer saturated in O_2. The calculation of AOU is in general biased to higher values, because in polar regions surface water leaves the surface water in respect to oxygen in a undersaturated state due to reduced air-sea gas transfer inhibited by sea ice (Ito et al., 2004). In UVic this leads to an overestimation of AOU by 30% (Duteil et al., 2013). For a warming ocean sea ice cover reduces which converts into an underestimation of the AOU anomaly in Fig. 9c. Changes in O_2 saturation were similar across the model simulations and followed with a delay surface ocean temperature. The circulation and ventilation of the ocean were similar in the model simulations because differences in surface temperatures were negligible and the atmospheric forcing of the ocean circulation was identical so that differences in AOU depended almost only on biological O_2 consumption and AOU anomalies were directly yet inversely related to the changes in O_2 levels. Hence, biological consumption explained variations in O_2 content among the different model simulations (compare Fig. 9a and 9b). Increasing O_2 utilization contributed to the decrease of the O_2 until the year 3000. Thereafter, a distinct negative trend in AOU with a similar slope was observed among all simulations and contributed to a re-oxygenation of the ocean. For simulations with larger P inventories, the AOU had a larger positive offset to the *Ref* simulation.

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

as anomalies). Preformed nutrients correspond to the fraction that leaves the surface ocean unutilized by phytoplankton. For example in the Southern Ocean, a large fraction of nutrients leaves the surface as preformed nutrients. The fraction of utilized and preformed nutrients can change during a transient simulation and could affect the oxygen state of the ocean.

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In the *Ref* simulation (Fig. 10a), the anomaly of preformed dissolved inorganic P was directly inverse to the anomaly of AOU because the oceanic P Inventory was conserved in this simulation. Until the year 2200, changes in circulation and climate are the main cause for the reduction in preformed N and P in the *Ref* simulation since global N and P inventories were almost constant in this time period (Fig 9a, solid red and black line). During continuous and intense ocean warming, a weakening of the meridional overturning (not shown) reduced ocean ventilation. The meridional overturning maximum decreased from 17 Sv (pre-industrial) to 11 Sv in the year 2200. The continuous warming and stratification of the ocean reduces the supply of nutrients to the surface layer from the deep ocean. This is consistent with a reduction of the export of organic matter until the year 2200 (Fig. 6b). The balance between exported P out of the surface ocean and supplied P controls changes in AOU. We speculate that a weaker overturning increased the residence time of water and nutrients in the surface ocean. Nutrients staying longer in the euphotic zone are with a higher probability biologically consumed. This implies more efficient utilization of nutrients and, hence, the reduction in preformed nutrients and an increase in AOU.

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Enhanced suboxia after the year 2200 drove excess denitrification and a decline in nitrate (Fig. 10a red solid line) in the *Ref* simulation. The decline in nitrate could explain the negative trend in AOU anomalies (Fig. 10a blue solid line) and therefore a negative feedback on the global deoxygenation. In the year 2200, overturning had started to recover quickly and increased to 21 Sv in the year 3000 (+24% relative to preindustrial values), which drove a faster overturning of organic matter in the surface ocean and a decrease in global AOU. We assume that the slight increase in export by 5% (relative to preindustrial values) was not strong enough to compensate for the by +24% faster overturning, which reduced the residence time of nutrients in the surface ocean.

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P addition in the *Weath0.15* simulation stimulated N_2-fixation by diazotrophs and counteracted N-loss by denitrification (Fig. 10b, red solid line). This led to an increase in N inventory by 17 Pmol O_2-equivalents compared to the *Ref* simulation. Furthermore, the high availability of P seems to reduce preformed N by 6 Pmol O_2 equivalents. Both explain the difference in AOU between *Weath0.15* and *Ref* of 24 Pmol O_2 at the end of the simulation (Fig. 9b). However, denitrification still exceeded N_2-fixation, which led to low levels of nitrate. From the year 5000 approximately all of the added P in the *Weath0.15* simulation remained unused by phytoplankton, left at the surface ocean as preformed P and was afterwards stored in the deep ocean. Phytoplankton was not able to utilize the extra P because it was limited in nitrate. Diazotrophs were not able to compensate for the lack in N due to iron limitation and low surface temperatures in the polar oceans. The denitrification feedback driven by the spread of suboxic conditions in the tropics had reduced further N availability for the phytoplankton and reduced the effect of P addition on the global oxygen level.

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5. Discussion and Conclusions

The P inventory is very sensitive to the weathering and benthic flux parameterizations tested in our model. Large uncertainties (Fig. 2, blue lines) derive from poorly constrained estimate for the preindustrial P weathering flux that ranges from 0.05 to 0.30 Tmol P a^{-1} (Benitez-Nelson, 2000; Compton et al., 2000; Ruttenberg, 2003). The preindustrial weathering flux in simulation *Weath0.15* (0.15 Tmol P a^{-1}) is well in this range. In this simulation, enhanced weathering leads to an increase in the global ocean P inventory by 25% until the year 5000 (Fig. 2, blue dotted line). Benthic fluxes of P were simulated using transfer functions on a subgrid bathymetry. Applying the transfer functions without taking into account the local sedimentary P inventory can greatly overestimate the release of benthic P on long time scales. In the UVic model, the application of finite benthic P inventories limited the benthic release significantly. Under low-oxygen conditions, sediments were P depleted already after a few years to decades. In our simulation, this resulted in an increase in the global oceanic P inventory by just 3% (Fig. 2, magenta solid line). This could imply that benthic release of P is actually negligible in comparison to the weathering fluxes of P, but the UVic model does not resolve coastal processes such as the deposition of reactive particulate P from rivers on the continental shelves and its dissolution and release to the water column. For a more realistic comparison of benthic and fluvial P fluxes, a more detailed representation of coastal processes would be necessary to simulate deposition and release of fluvial P from the sediments at the shelf. However, we can conclude that the actual local inventories of P are too small to sustain a positive benthic P feedback over several millennial. Further, we find that a more realistic bathymetry substantially improves the simulated rain rate of particular organic carbon to the sediment (Table 2), particularly on the shelf, which most models do not resolve. Anthropogenic P fluxes increased the global P inventory by just 2% (Fig. 2, black dashed line). In summary, our best estimate for changes in the total global ocean P inventory by the year 5000 amounts to +30%, which was dominated by weathering. This seems to be surprisingly high, but several studies indicate that changes in past climate could also have been accompanied with substantial changes in the P inventory but at a much lower pace (Planavsky et al., 2010; Monteiro et al., 2012; Wallmann, 2014). In this simple addition of the P inventories we cannot account for feedbacks, which would appear in a fully coupled model. For such high P inventories we would expect larger suboxia and therefore more P release from sediments and at the same time a stronger export of organic P that lead to increased P burial.

The increased P inventory (Fig. 2b) promotes deoxygenation (Fig. 5) and expansion of suboxia, but it also causes a net loss of nitrate, which appears to further limit the full utilization of P by phytoplankton in our simulations. Wallmann (2003), using a box model, already recognized that for a eutrophic ocean, nitrate might ultimately limit marine productivity. As a consequence, large amounts of P leave the surface ocean as preformed P (Fig. 10b) with no further impact on O_2 levels in the ocean interior. Low N/P ratios are thought to give N_2-fixers a competitive advantage over ordinary phytoplankton and lead to an increase in N_2-fixation (Fig. 7a). In the time period of the OAE1a and the OAE2, a substantial increase in N_2-fixation was also inferred from measurements of sediment nitrogen isotope compositions typical for newly fixed nitrogen conditions and from high abundances of cyanobacteria indicated by a high 2-methylhopanoid index (Kuypers et al., 2004). However, high denitrification rates

remove nitrate from the global ocean and in the UVic model N_2-fixers are not able to compensate for this loss (Fig. 7b) because low temperatures in polar regions and iron limitation at lower latitudes inhibit growth of diazotrophs (Fig. 8) and a substantial amount of excess phosphate remains in the surface waters in these regions (Fig. S2). General circulation models without a N cycle, or box models without realistic representation of habitats suitable for N_2-fixers, would miss this important negative feedback limiting global deoxygenation. As a next step it would be reasonable to investigate how different parameterizations of the N cycle and a full dynamic iron cycle will affect the utilization of the added P. For example benthic denitrification is not simulated in the UVic model. Model simulations showed for this century, that the enhanced denitrification in the water column could be compensated by less benthic denitrification (Landolfi et al., 2017), which could reduce the N-limitation and therefore enhance the effect of P fluxes on the biological pump. Sources of bioavailable Fe are still not well quantified and how these sources change under climate change is under debate (Hutchins et al., 2016; Mahowald et al., 2005). A more realistic representation of a dynamic iron cycle in UVic would affect N_2-fixation in many areas of the global ocean (Fig. 8).

Some additional model limitations are a cause for uncertainty in our results. We considered a fixed Redfield-ratio stoichiometry. In future deoxygenation studies, an optimality-based model for nutrient uptake with variable nutrient ratios (Pahlow et al., 2013) could be applied to investigate how well marine organisms adapt to a changing nutrient availability in the global ocean. Sea level change and the implied bathymetry change were not simulated in the UVic model. In future projections, higher surface air temperatures would lead to a rise in sea level, which increase global coverage of shelf areas. Burial of P is more effective on the shelf (Flögel et al., 2011), which would remove P from the ocean and lead to a lower marine P residence time (Bjerrum et al., 2006).

To conclude, climate warming leads to a larger oceanic P inventory mainly due to addition of P by weathering, but also due to the release of P from the sediment and due to anthropogenic fluxes. A realistic representation of shelf bathymetry improves the predicted benthic P fluxes. Transfer functions for benthic P release should consider the sedimentary P inventory. However, the largest uncertainties in the projection of oceanic P inventory are due to poorly constrained weathering fluxes of P. Although additional deoxygenation is driven by P addition to the ocean, the degree of deoxygenation – and hence the positive redox-related feedback on benthic P release is eventually limited by the availability of N and the apparent inability of the modelled N_2 fixation to respond to the larger P inventory.

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Data and Code Availability. The model data and the model code are available at https://data.geomar.de/thredds/catalog/open_access/kemena_et_al_2018_esd/catalog.html.

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

Bibliography:

Archer, D.: A data driven model of the global calcite lysocline, Global Biogeochem. Cycles, 10, 511–
526, doi: 10.1029/96GB01521, 1996.

Baturin, G. N.: Issue of the relationship between primary productivity of organic carbon in ocean and
phosphate accumulation (Holocene-Late Jurassic). Lithol. Miner. Resour., 42, 318–348, doi:
10.1134/S0024490207040025, 2007.

Bauer, K. W., Zeebe, R. E., and Wortmann, U. G.: Quantifying the volcanic emissions which triggered
Oceanic Anoxic Event 1a and their effect on ocean acidification, Sedimentology, 64, 204–214,
doi: 10.1111/sed.12335, 2017.

Benitez-Nelson, C. R.: The biogeochemical cycling of phosphorus in marine systems, Earth. Sci. Rev.,
51, 109–135, doi: 10.1016/S0012-8252(00)00018-0, 2000.

Beusen, A. H. W., Bouwman, A. F., Van Beek, L. P. H., Mogollón, J. M., and Middelburg, J. J.: Global
riverine N and P transport to ocean increased during the 20th century despite increased retention
along the aquatic continuum, Biogeosciences, 13, 2441–2451, doi: 10.5194/bg-13-2441-2016,
2016.

Bitz, C. M., and Lipscomb, W. H.: An energy-conserving thermodynamic model of sea ice, J. Geophys.
Res., 104, 15669, doi: 10.1029/1999JC900100, 1999.

Bjerrum, C. J., Bendtsen, J., and Legarth, J. J. F.: Modeling organic carbon burial during sea level rise
with reference to the Cretaceous, Geochem. Geophys. Geosyst., 7, Q05008, doi:
10.1029/2005GC001032, 2006.

Blättler, C. L., Jenkyns, H. C., Reynard, L. M., and Henderson, G. M.: Significant increases in global
weathering during Oceanic Anoxic Events 1a and 2 indicated by calcium isotopes, Earth Planet
Sci. Lett., 309, 77–88, doi: 10.1016/j.epsl.2011.06.029, 2011.

Bohlen, L., Dale, A. W., and Wallmann, K.: Simple transfer functions for calculating benthic fixed
nitrogen losses and C:N:P regeneration ratios in global biogeochemical models. Global
Biogeochem. Cycles, 26, GB3029, doi: 10.1029/2011GB004198, 2012.

Bopp, L., Le Quéré, C., Heimann, M., Manning, A. C., Monfray, P.: Climate-induced oceanic oxygen
fluxes: Implications for the contemporary carbon budget, Global Biogeochem. Cycles, 16, 6-1-6-
13, doi: 10.1029/2001GB001445, 2002.

Burdige, D. J.: Preservation of organic matter in marine sediments: Controls, mechanisms, and an
imbalance in sediment organic carbon budgets? Chem. Rev., 107, 467–485, doi:
10.1021/cr050347q, 2007.

Burwicz, E. B., Rüpke, L. H., and Wallmann, K.: Estimation of the global amount of submarine gas
hydrates formed via microbial methane formation based on numerical reaction-transport
modeling and a novel parameterization of Holocene sedimentation. Geochim. Cosmochim. Acta.,
75, 4562–4576, doi: 10.1016/j.gca.2011.05.029, 2011.

Clark, P. U., Shakun, J. D., Marcott, S. A., Mix, A. C., Eby, M., Kulp, S., Levermann, A., Milne, G. A.,
Pfister, P. L., Santer, B. D., Schrag, D. P., Solomon, S., Stocker, T. F., Strauss, B. H., Weaver, A.
J., Winkelmann, R., Archer, D., Bard, E., Goldner, A., Lambeck, K., Pierrehumbert, R. T., and
Plattner, G.-K.: Consequences of twenty-first-century policy for multi-millennial climate and sea-

level change, Nat. Clim. Chang., 6, 360–369, doi: 10.1038/nclimate2923, 2016.

Compton, J., Mallinson, D., Glenn, C. R., Filippelli, G., Föllmi, K., Shields, G., and Zanin, Y.:
570   Variations in the global phosphorus cycle, Marine Authigenesis: From Global to Microbial,
edited by: Glenn, C. R., Prévôt, L., and Lucas, J., SEPM Spec. Publ., 66, 21–33, doi:
10.2110/pec.00.66.0021, 2000

Damsté, J. S. S., Kuypers, M. M. M., Pancost, R. D., and Schouten, S.: The carbon isotopic response of
algae, (cyano)bacteria, archaea and higher plants to the late Cenomanian perturbation of the
575   global carbon cycle: Insights from biomarkers in black shales from the Cape Verde Basin (DSDP
Site 367), Org. Geochem., 39, 1703–1718, doi: 10.1016/j.orggeochem.2008.01.012, 2008.

Dunne, J. P., Sarmiento, J. L., and Gnanadesikan, A.: A synthesis of global particle export from the
surface ocean and cycling through the ocean interior and on the seafloor, Global Biogeochem.
Cycles, 21, 1–16, doi: 10.1029/2006GB002907, 2007.

580 Duteil, O., Koeve, W., Oschlies, A., Bianchi, D., Galbraith, E., Kriest, I., and Matear, R.: A novel
estimate of ocean oxygen utilisation points to a reduced rate of respiration in the ocean interior,
Biogeosciences, 10, 7723–7738, doi: 10.5194/bg-10-7723-2013, 2013.

Eby, M., Weaver, A. J., Alexander, K., Zickfeld, K., Abe-Ouchi, A., Cimatoribus, A. A., Crespin, E.,
Drijfhout, S. S., Edwards, N. R., Eliseev, A. V., Feulner, G., Fichefet, T., Forest, C. E., Goosse,
585   H., Holden, P. B., Joos, F., Kawamiya, M., Kicklighter, D., Kienert, H., Matsumoto, K., Mokhov,
I. I., Monier, E., Olsen, S. M., Pedersen, J. O. P., Perrette, M., Philippon-Berthier, G., Ridgwell,
A., Schlosser, A., Schneider von Deimling, T., Shaffer, G., Smith, R. S., Spahni, R., Sokolov, A.
P., Steinacher, M., Tachiiri, K., Tokos, K., Yoshimori, M., Zeng, N., and Zhao, F.: Historical and
idealized climate model experiments: an intercomparison of Earth system models of intermediate
590   complexity, Clim. Past, 9, 1111–1140, doi: 10.5194/cp-9-1111-2013, 2013.

Fanning, A. F., and Weaver, A. J.: An atmospheric energy-moisture balance model: Climatology,
interpentadal climate change, and coupling to an ocean general circulation model, J. Geophys.
Res., 101, 15111, doi: 10.1029/96JD01017, 1996.

Filippelli, G. M.: Carbon and phosphorus cycling in anoxic sediments of the Saanich Inlet, British
595   Columbia, Mar. Geol., 174, 307–321, doi: 10.1016/S0025-3227(00)00157-2, 2001.

Filippelli, G. M.: The Global Phosphorus Cycle, Rev. Mineral. Geochemistry, 48, 391–425, doi:
10.2138/rmg.2002.48.10, 2002.

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

600 Filippelli, G. M., and Delaney, M. L.: Phosphorus geochemistry of equatorial Pacific sediments,
Geochim. Cosmochim. Acta., 60, 1479–1495, doi: 10.1016/0016-7037(96)00042-7, 1996.

Flögel, S., Wallmann, K., Poulsen, C. J., Zhou, J., Oschlies., A., Voigt, S., and Kuhnt, W.: Simulating
the biogeochemical effects of volcanic CO_2 degassing on the oxygen-state of the deep ocean
during the Cenomanian/Turonian Anoxic Event (OAE2), Earth Planet Sci. Lett., 305, 371–384,
605   doi: 10.1016/j.epsl.2011.03.018, 2011.

Getzlaff, J., Dietze, H., and Oschlies, A.: Simulated effects of southern hemispheric wind changes on
the Pacific oxygen minimum zone, Geophys. Res. Lett., 43, 728–734, doi:

10.1002/2015GL066841, 2016.

Harrison, J. A., Beusen, A. H., Fink, G., Tang, T., Strokal, M., Bouwman, A. F., Metson, G. S., and
610   Vilmin, L.: Modeling phosphorus in rivers at the global scale: recent successes, remaining
challenges, and near-term opportunities, Curr. Opin. Environ. Sustain., 36, 68–77, doi:
10.1016/j.cosust.2018.10.010, 2019.

Hartmann, J., Moosdorf, N., Lauerwald, R., Hinderer, M., and West, A. J.: Global chemical weathering
and associated P-release - The role of lithology, temperature and soil properties, Chem. Geol.,
615   363, 145–163, doi: 10.1016/j.chemgeo.2013.10.025, 2014.

Hutchins, D. A., and Boyd, P. W.: Marine phytoplankton and the changing ocean iron cycle, Nat. Clim.
Chang., 6, 1072–1079, doi: 10.1038/nclimate3147, 2016.

Ingall, E., and Jahnke, R.: Evidence for enhanced phosphorus regeneration from marine sediments
overlain by oxygen depleted waters, Geochim. Cosmochim. Acta., 58, 2571–2575, doi:
620   10.1016/0016-7037(94)90033-7, 1994.

Ito, T., Follows, M. J., and Boyle, E. A.: Is AOU a good measure of respiration in the oceans?
Geophys. Res. Lett., 31, L17305, doi: 10.1029/2004GL020900, 2004.

Jones CE, Jenkyns HC (2001) Seawater strontium isotopes, oceanic anoxic events, and seafloor
hydrothermal activity in the Jurassic and Cretaceous. Am J Sci 301:112–149. doi:
625   10.2475/ajs.301.2.112

Keller, D. P., Oschlies, A., and Eby, M.: A new marine ecosystem model for the University of Victoria
Earth System Climate Model, Geosci. Model Dev., 5, 1195–1220, doi: 10.5194/gmd-5-1195-
2012, 2012.

Keller, D. P., Kriest, I., Koeve, W., and Oschlies, A.: Southern Ocean biological impacts on global
630   ocean oxygen, Geophys. Res. Lett., 43, 6469–6477, doi: 10.1002/2016GL069630, 2016.

Kidder, D. L., and Worsley, T. R.: Phanerozoic Large Igneous Provinces (LIPs), HEATT (Haline
Euxinic Acidic Thermal Transgression) episodes, and mass extinctions, Palaeogeogr.
Palaeoclimatol. Palaeoecol., 295, 162–191, doi: 10.1016/j.palaeo.2010.05.036, 2010.

Kidder, D. L., and Worsley, T. R.: A human-induced hothouse climate?, GSA Today, 22, 4–11, doi:
635   10.1130/G131A.1, 2012.

Kraal, P., Slomp, C. P., Forster, A., and Kuypers, M. M. M.: Phosphorus cycling from the margin to
abyssal depths in the proto-Atlantic during oceanic anoxic event 2, Palaeogeogr. Palaeoclimatol.
Palaeoecol., 295, 42–54, doi: 10.1016/j.palaeo.2010.05.014, 2010.

Kuypers, M. M. M., van Breugel, Y., Schouten, S., Erba, E., and Damsté, J. S. S.: N2-fixing
640   cyanobacteria supplied nutrient N for Cretaceous oceanic anoxic events, Geology, 32, 853–856,
doi: 10.1130/G20458.1, 2004.

Landolfi, A., Dietze, H., Koeve, W., and Oschlies, A.: Overlooked runaway feedback in the marine
nitrogen cycle: The vicious cycle, Biogeosciences, 10, 1351–1363, doi: 10.5194/bg-10-1351-
2013, 2013.

645   Landolfi, A., Somes, C. J., Koeve, W., Zamora, L. M., and Oschlies, A.: Oceanic nitrogen cycling and
N 2 O flux perturbations in the Anthropocene, Global Biogeochem. Cycles, 31, 1–20. doi:
10.1002/2017GB005633, 2017.

Lenton, T. M., and Britton, C.: Enhanced carbonate and silicate weathering accelerates recovery from fossil fuel CO2 perturbations, Global Biogeochem. Cycles, 20, 1–12, doi: 10.1029/2005GB002678, 2006.

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

Mahowald, N. M., Baker, A. R., Bergametti, G., Brooks, N., Duce, R. A., Jickells, T. D., Kubilay, N., Prospero, J. M., and Tegen, I.: Atmospheric global dust cycle and iron inputs to the ocean, Global Biogeochem. Cycles, doi: 10.1029/2004GB002402, 2005.

Martin, J. M., and Meybeck, M.: Elemental mass balance of material carried by major world rivers, Mar. Chem., 7, 173-206, 1979.

Matear, R. J., and Hirst A. C.: Long-term changes in dissolved oxygen concentrations in the ocean caused by protracted global warming, Global Biogeochem. Cycles, 17(4), 1125, doi: 10.1029/2002GB001997, 2003.

Méhay, S., Keller, C. E., Bermasconi, S. M., Weissert, H., Erba, E., Bottini, C., and Hochuli, P. A.: A volcanic CO2 pulse triggered the Cretaceous oceanic Anoxic event 1a and a biocalcification crisis, Geology, 37, 819–822, doi: 10.1130/G30100A.1, 2009.

Meinshausen, M., Smith, S. J., Calvin, K., Daniel, J. S., Kainuma, M. L. T., Lamarque, J., Matsumoto, K., Montzka, S. A., Raper, S. C. B., Riahi, K., Thomson, A., Velders, G. J. M., and van Vuuren, D. P. P.: The RCP greenhouse gas concentrations and their extensions from 1765 to 2300, Clim. Change, 109, 213–241, doi: 10.1007/s10584-011-0156-z, 2011.

Meissner, K. J., Weaver, A. J., Matthews, H. D., and Cox, P. M.: The role of land surface dynamics in glacial inception: a study with the UVic Earth System Model, Clim. Dyn., 21, 515–537, doi: 10.1007/s00382-003-0352-2, 2003.

Meissner, K. J., McNeil, B. I., Eby, M., and Wiebe, E. C.: The importance of the terrestrial weathering feedback for multimillennial coral reef habitat recovery, Global Biogeochem. Cycles, 26, 1–20, doi: 10.1029/2011GB004098, 2012.

Monteiro, F. M., Pancost, R. D., Ridgwell, A., and Donnadieu, Y.: Nutrients as the dominant control on the spread of anoxia and euxinia across the Cenomanian-Turonian oceanic anoxic event (OAE2): Model-data comparison, Paleoceanography, 27, 1–17, doi: 10.1029/2012PA002351, 2012.

Mort, H. P., Adatte, T., Föllmi, K. B., Keller, G., Steinmann, P., Matera, V., Berner, Z., and Stüben, D.: Phosphorus and the roles of productivity and nutrient recycling during oceanic anoxic event 2, Geology, 35, 483–486, doi: 10.1130/G23475A.1, 2007.

Muller-Karger, F. E., Varela, R., Thunell, R., Luerssen, R., Hu, C., and Walsh, J. J.: The importance of continental margins in the global carbon cycle, Geophys. Res. Lett., 32, 1–4, doi: 10.1029/2004GL021346, 2005.

National Geophysical Data Center, . 2-minute Gridded Global Relief Data (ETOPO2) v2, National Geophysical Data Center, NOAA, doi:10.7289/V5J1012Q, 2006.

Nickelsen, L., Keller, D. P., and Oschlies, A.: A dynamic marine iron cycle module coupled to the University of Victoria Earth System Model: The Kiel Marine Biogeochemical Model 2 for UVic 2.9, Geosci. Model Dev., 8, 1357–1381, doi: 10.5194/gmd-8-1357-2015, 2015.

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

Oschlies, A., Schulz, K. G., Riebesell, U., and Schmittner, A.: Simulated 21st century's increase in oceanic suboxia by CO_2-enhanced biotic carbon export, Global Biogeochem. Cycles, 22, 1–10, doi: 10.1029/2007GB003147, 2008.

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

Pacanowski, R. C.: MOM2: Documentation, User's Guide and Reference Manual, GFDL Ocean Tech. Rep. 3.2, 1996.

Pahlow, M., Dietze, H., and Oschlies, A.: Optimality-based model of phytoplankton growth and diazotrophy, Mar. Ecol. Prog. Ser., 489, 1–16, doi: 10.3354/meps10449, 2013.

Palastanga, V., Slomp, C. P., and Heinze, C.: Long-term controls on ocean phosphorus and oxygen in a global biogeochemical model, Global Biogeochem. Cycles, 25, 1–19, doi: 10.1029/2010GB003827, 2011.

Planavsky, N. J., Rouxel, O. J., Bekker, A., Lalonde, S. V., Konhauser, K. O., Reinhard, C. T., and Lyons, T. W.: The evolution of the marine phosphate reservoir, Nature, 467, 1088–1090, doi: 10.1038/nature09485, 2010.

Pogge von Strandmann, P. A. E., Jenkyns, H. C., and Woodfine, R. G.: Lithium isotope evidence for enhanced weathering during Oceanic Anoxic Event 2, Nat. Geosci., 6, 668–672, doi: 10.1038/ngeo1875, 2013.

Rao, J., and Berner, R.: Phosphorus dynamics in the Amazon river and estuary, Chem. Geol., 107, 397–400, doi: 10.1016/0009-2541(93)90218-8, 1993.

Ruttenberg, K. C.: The Global Phosphorus Cycle. Treatise on Geochemistry, edited by: Schlesinger, W., Elsevier, 585–643, doi: 10.1016/B0-08-043751-6/08153-6, 2003.

Ruvalcaba Baroni, I., Topper, R. P. M., Van Helmond, N. A. G. M., Brinkhuis, H., and Slomp C. P.: Biogeochemistry of the North Atlantic during oceanic anoxic event 2: Role of changes in ocean circulation and phosphorus input, Biogeosciences, 11, 977–993, doi: 10.5194/bg-11-977-2014, 2014.

Saltzman, M. R.: Phosphorus, nitrogen, and the redox evolution of the Paleozoic oceans, Geology, 33, 573–576, doi: 10.1130/G21535.1, 2005.

Schmittner, A., Galbraith, E. D., Hostetler, S. W., Pedersen, T. F., and Zhang, R.: Large fluctuations of dissolved oxygen in the Indian and Pacific oceans during Dansgaard-Oeschger oscillations caused by variations of North Atlantic Deep Water subduction, Paleoceanography, 22, 1–17, doi: 10.1029/2006PA001384, 2007.

Shaffer, G., Olsen, S. M., and Pedersen, J. O. P.: Long-term ocean oxygen depletion in response to carbon dioxide emissions from fossil fuels, Nat. Geosci., 2, 105–109, doi: 10.1038/ngeo420, 2009.

Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., and Bouwman, A. F.: Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient

Export from Watersheds (NEWS) models and their application, Global Biogeochem. Cycles, 19, 1–11, doi: 10.1029/2005GB002606, 2005.

730 Seitzinger, S. P., Mayorga, E., Bouwman, A. F., Kroeze, C., Beusen, A. H. W., Billen, G., Van Drecht, G., Dumont, E., Fekete, B. M., Garnier, J., and Harrison, J. A.: Global river nutrient export: A scenario analysis of past and future trends, Global Biogeochem. Cycles, 24, 1-16, doi: 10.1029/2009GB003587, 2010.

Somes, C. J., Oschlies, A., and Schmittner, A.: Isotopic constraints on the pre-industrial oceanic
735 nitrogen budget, Biogeosciences, 10, 5889–5910, doi: 10.5194/bg-10-5889-2013, 2013.

Tsandev, I., and Slomp, C. P.: Modeling phosphorus cycling and carbon burial during Cretaceous Oceanic Anoxic Events, Earth Planet Sci. Lett., 286, 71–79, doi: 10.1016/j.epsl.2009.06.016, 2009.

Tyrrell T.: The relative influences of nitrogen and phosphorus on oceanic primary production, Nature,
740 400, 525–531, doi: 10.1038/22941, 1999.

Van Cappellen, P., and Ingall, E. D.: Benthic phosphorous regeneration, net primary production, and ocean anoxia: a model of the couple biogeochemical cycles of carbon and phosphorous, Paleooceanography, 9, 667–692, doi: 10.1029/94PA01455, 1994.

Wallmann, K.: Feedbacks between oceanic redox states and marine productivity: A model perspective
745 focused on benthic phosphorus cycling, Global Biogeochem. Cycles, 17, doi: 10.1029/2002GB001968, 2003.

Wallmann, K.: Phosphorus imbalance in the global ocean?, Global Biogeochem. Cycles, 24, 1–12, doi: 10.1029/2009GB003643, 2010.

Wallmann, K.: Is late Quaternary climate change governed by self-sustained oscillations in
750 atmospheric CO2?, Geochim. Cosmochim. Acta., 132, 413–439, doi: 10.1016/j.gca.2013.10.046, 2014.

Watson, A. J., Lenton, T. M., and Mills, B. J. W.: Ocean deoxygenation, the global phosphorus cycle and the possibility of human-caused large-scale ocean anoxia, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci., 375, 20160318, doi: 10.1098/rsta.2016.0318, 2017.

755 Weaver, A. J., Eby, M., Wiebe, E. C., Bitz, C. M., Duffy, P. B., Ewen, T. L., Fanning, A. F., Holland, M. M., MacFadyen, A., Matthews, H. D., Meissner, K. J., Saenko, O., Schmittner, A., Wang, H., and Yoshimori, M.: The UVic earth system climate model: Model description, climatology, and applications to past, present and future climates, Atmosphere-Ocean, 39, 361–428, doi: 10.1080/07055900.2001.9649686, 2001.

760 Withers, P. J. A., and Jarvie, H. P.: Delivery and cycling of phosphorus in rivers: A review, Sci. Total Environ., 400, 379–395, doi: 10.1016/j.scitotenv.2008.08.002, 2008.

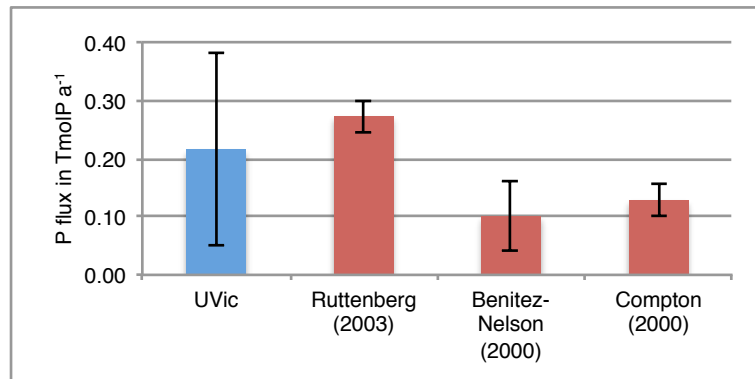
Tables:

Table 1: Overview of simulations. P fluxes are given in TmolP a^{-1}. We divided all simulations in four groups indicated by different colors. These are: reference simulations (in black) with and without anthropogenic fluxes of P; simulations with different formulations for the burial (in red beginning with the acronym Bur); simulations with weathering fluxes of P for different climate sensitivities (in blue beginning with the acronym Weath); and simulations with different representations of the sediment (in purple). In the P weathering simulations, only weathering anomalies were applied. The weathering flux in simulation *Anthr* is variable over time (Fig. 2a). In the P burial simulations, a constant P weathering flux ($W_{P,0}$) balances P burial (BUR$_P$) during the spin-up simulations. The preindustrial P inventory is identical in all simulations. More detailed information can be found in the text.

Simulations	Abbreviation	Fluxes	P Burial parametrization
Reference (constant P inv.)	*Ref*	No	No burial
Anthropogenic P input	*Anthr*	Flux from Filippelli (2008)	No burial
Burial Reference	*Bur*	BUR_P (t=1775a)=0.38 $W_{P,const}$=0.38	$r_{C:P}$ (Wallmann, 2010), C Burial (Flögel et al., 2011) Y_F=123; A=112; r=32 in Eq. 4
Burial Dunne	*Bur_Dun*	BUR_P (t=1775a)=0.25 $W_{P,const}$=0.25	$r_{C:P}$ (Wallmann, 2010), C Burial (Dunne et al., 2007)
Low burial estimate	*Bur_low*	BUR_P (t=1775a)=0.21 $W_{P,const}$=0.21	*Bur* configuration, but with Y_F=100.5; A=90; r=38 in Eq. 4
High burial estimate	*Bur_high*	BUR_P (t=1775a)=0.60 $W_{P,const}$=0.60	*Bur* configuration, but with Y_F=167; A=108.5; r=29.5 in Eq. 4
Burial without subgrid bathymetry	*Bur_noSG*	BUR_P (t=1775a)=0.09 $W_{P,const}$=0.09	*Bur* configuration, but without subgrid bathymetry
Burial with restricted reservoir	*Bur_res*	BUR_P (t=1775a)=0.41 $W_{P,const}$=0.41	*Bur* configuration, but with 113 µmolP cm^{-2} Reservoir
Weathering	*Weath0.05*	$W_{P,0}$=0.05	*No burial*
Weathering	*Weath0.10*	$W_{P,0}$=0.10	*No burial*
Weathering	*Weath0.15*	$W_{P,0}$=0.15	*No burial*
Weathering	*Weath0.38*	$W_{P,0}$=0.38	*No burial*

Table 2: Rain rate of particulate organic carbon (*RR_C*) to the seafloor for the shelf, slope and deep-sea areas from the observational estimate by Bohlen et al. (2012) and for the UVic model simulation *Bur* with and without subgrid bathymetry. Preindustrial RR_C shows no significant differences among all model simulations (expect for simulation *Bur_noSG*).

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

Figures:

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

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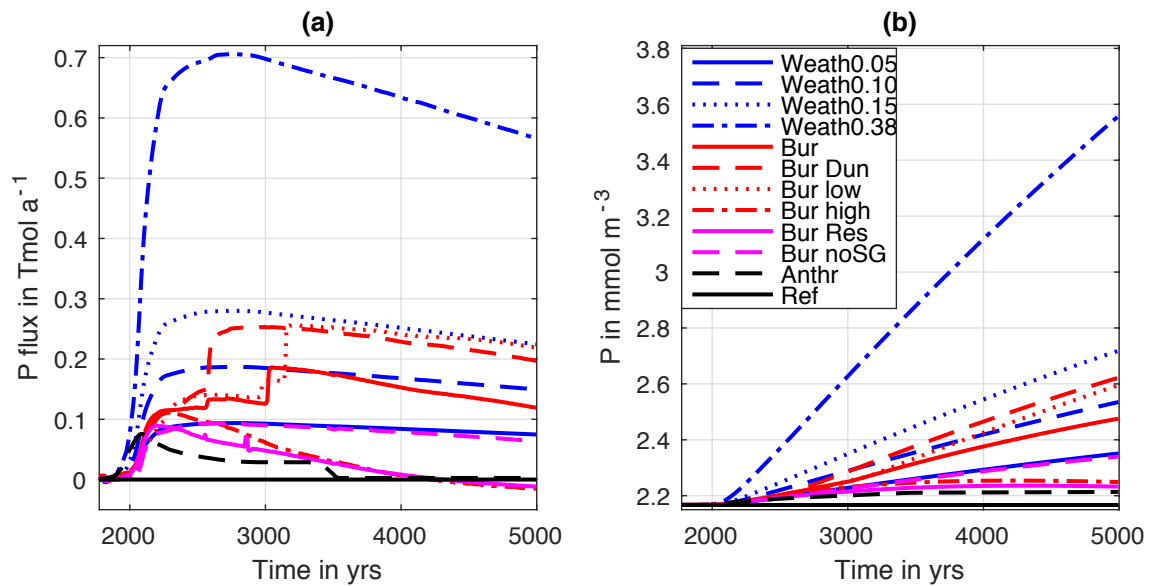


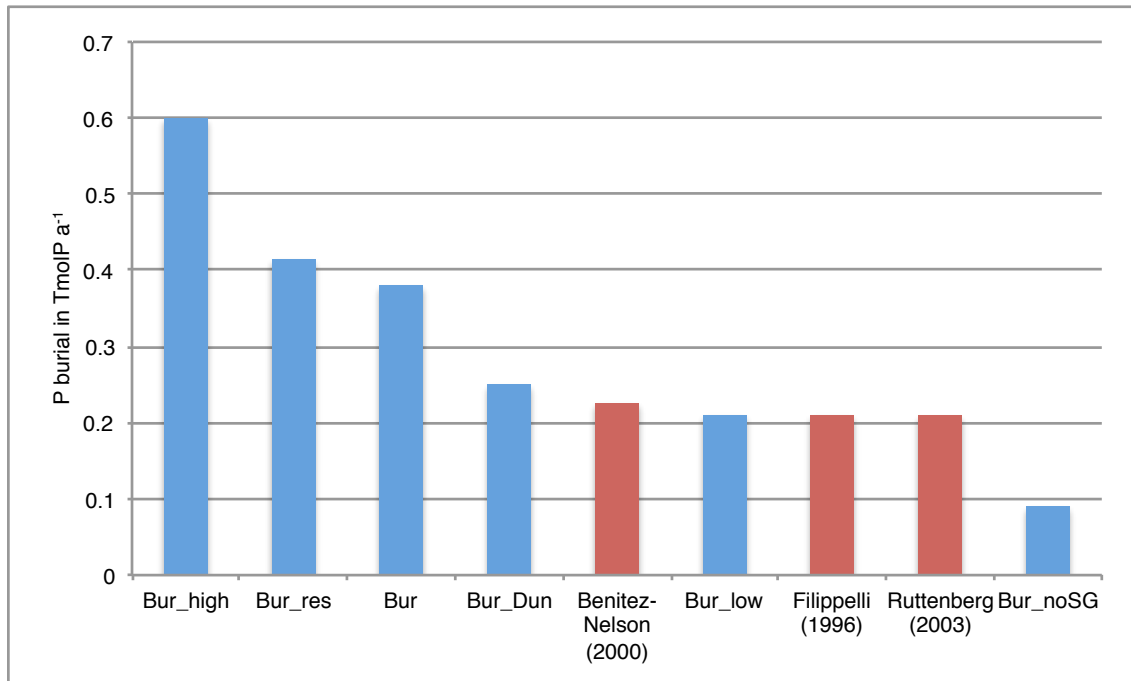
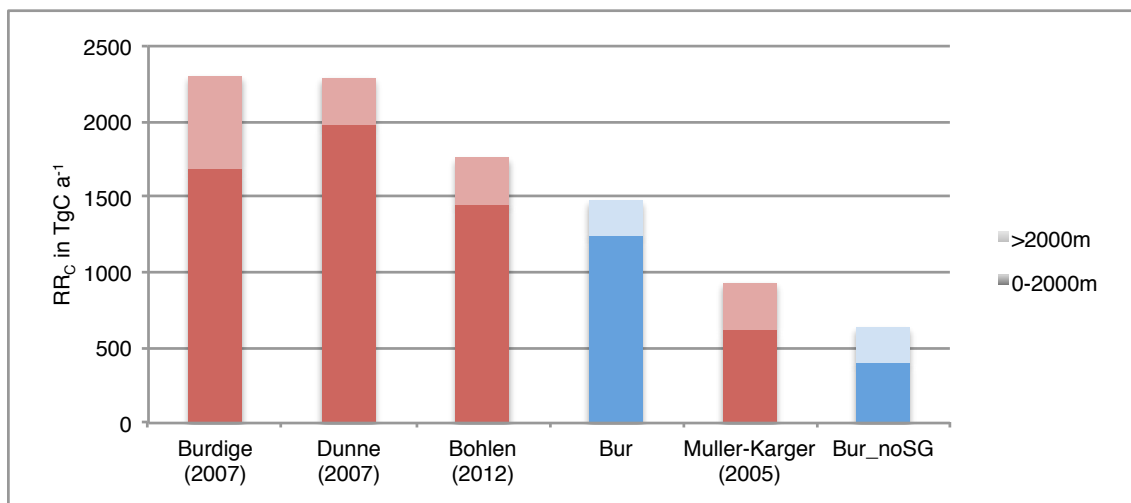
Fig. 2: (a) Globally integrated flux of P in Tmol a^{-1} to the ocean and (b) globally averaged phosphate concentration in mmol m^{-3}. Simulation descriptions can be found in Table 1.

800 **Fig. 3: Globally integrated preindustrial P burial fluxes in TmolP a⁻¹ from field studies (red) and for UVic model simulations in the year 1775 (blue). Description of the model simulations can be found in Table 1.**

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

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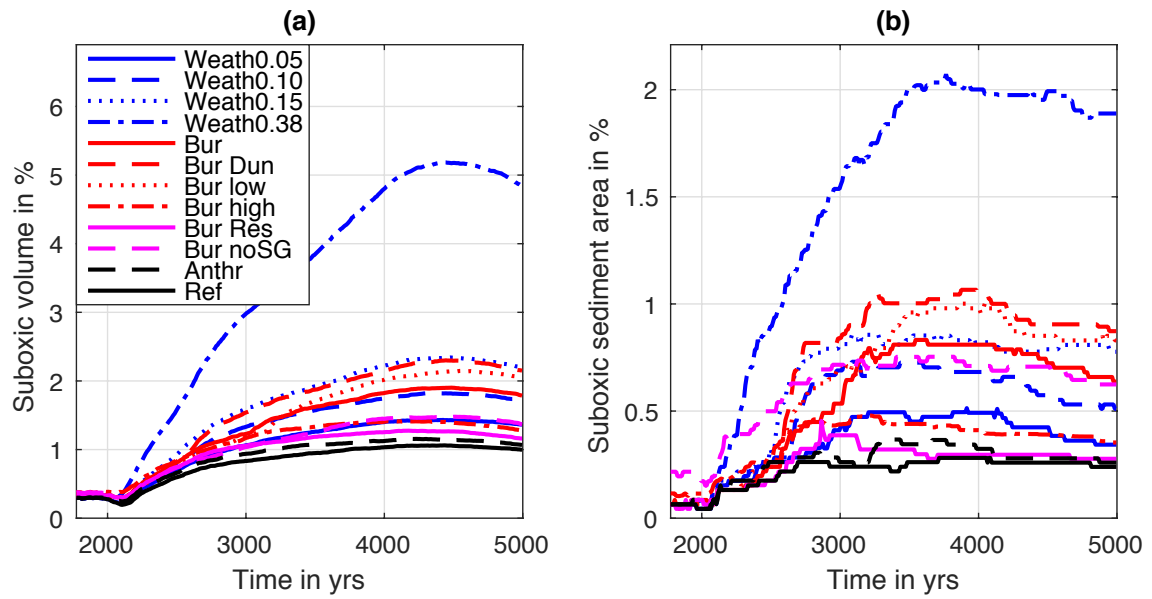
Fig. 5: Globally integrated (a) suboxic volume in percentage of total ocean volume and (b) suboxic sediment surface area in percentage of total sediment surface area. Water is designated as suboxic for oxygen concentrations below 5 mmolO$_2$ m^{-3}. Simulation descriptions can be found in Table 1.

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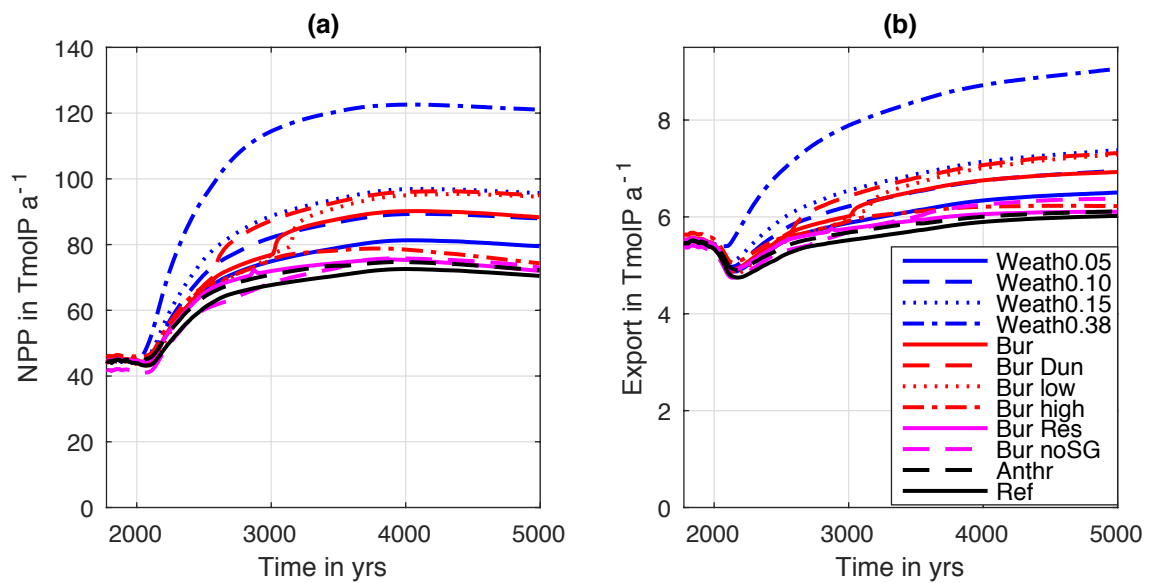
Fig. 6: Globally integrated (a) ocean net primary production (NPP) in TmolP a^{-1} and (b) export of organic P below the 130m depth level in TmolP a^{-1}. Simulation descriptions can be found in Table 1.

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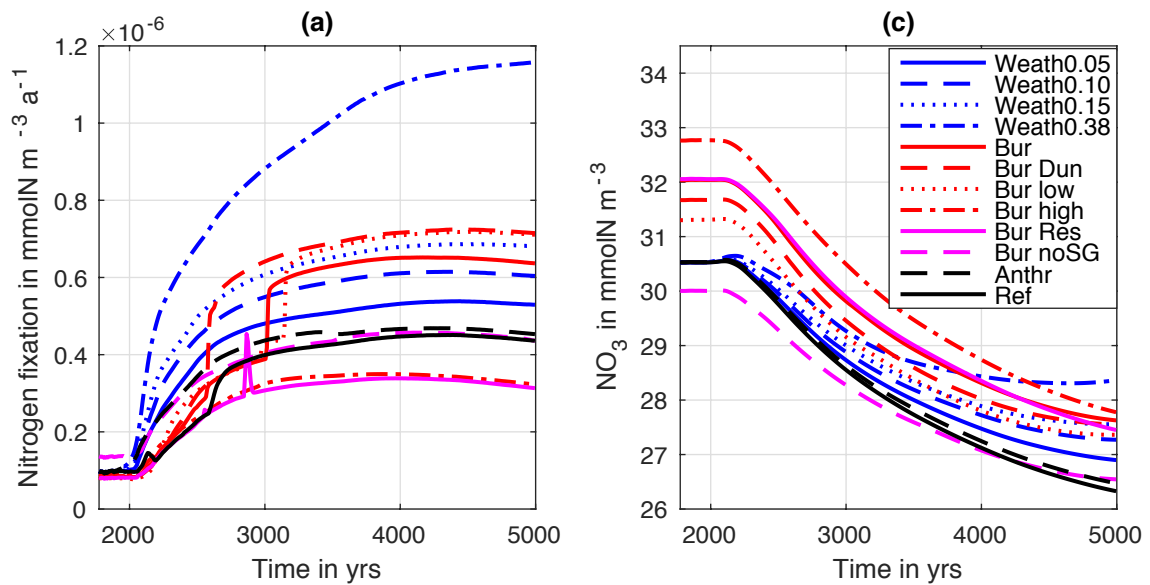
Fig. 7: Globally averaged (a) N$_2$-fixation in mmolN m^{-3} a^{-1} and (b) NO$_3^-$ concentration in mmolN m^{-3}. Simulation descriptions can be found in Table 1.

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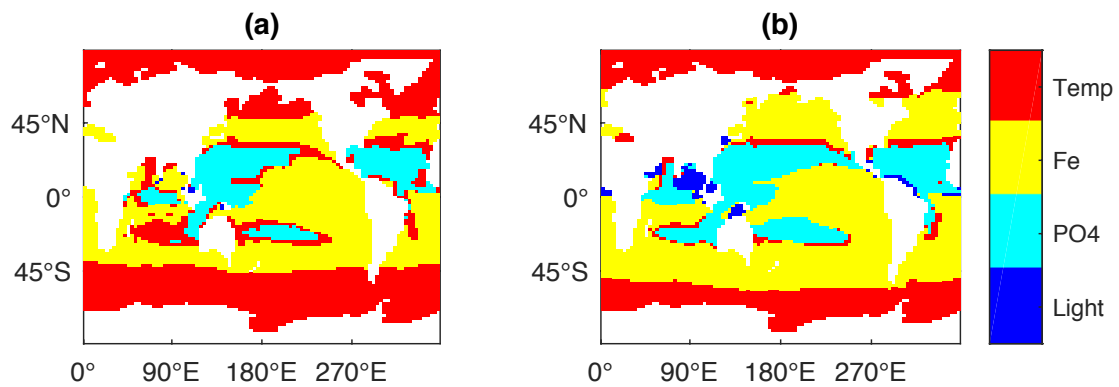
Fig. 8: Spatial distribution of the most limiting factors for growth of diazotrophs for (a) the preindustrial case and (b) simulation year 5000 for *Weath0.15*. Limitation of iron (Fe) and phosphate (PO4) are based on Monod kinetics so that the limitation factors vary between 0 and 1. The light limitation factor also varies between 0 and 1. In the model, diazotrophs only grow at temperatures higher than 15.7 °C. For

830   temperatures above 15.7 °C, diazotroph growth depends on the equation exp(T/15.7°C)-2.61. Diazotroph growth is not limited by nitrate availability in the model. A more detailed description of diazotroph growth and iron limitation can be found in Keller et al. (2012) and Nickelsen et al. (2015).
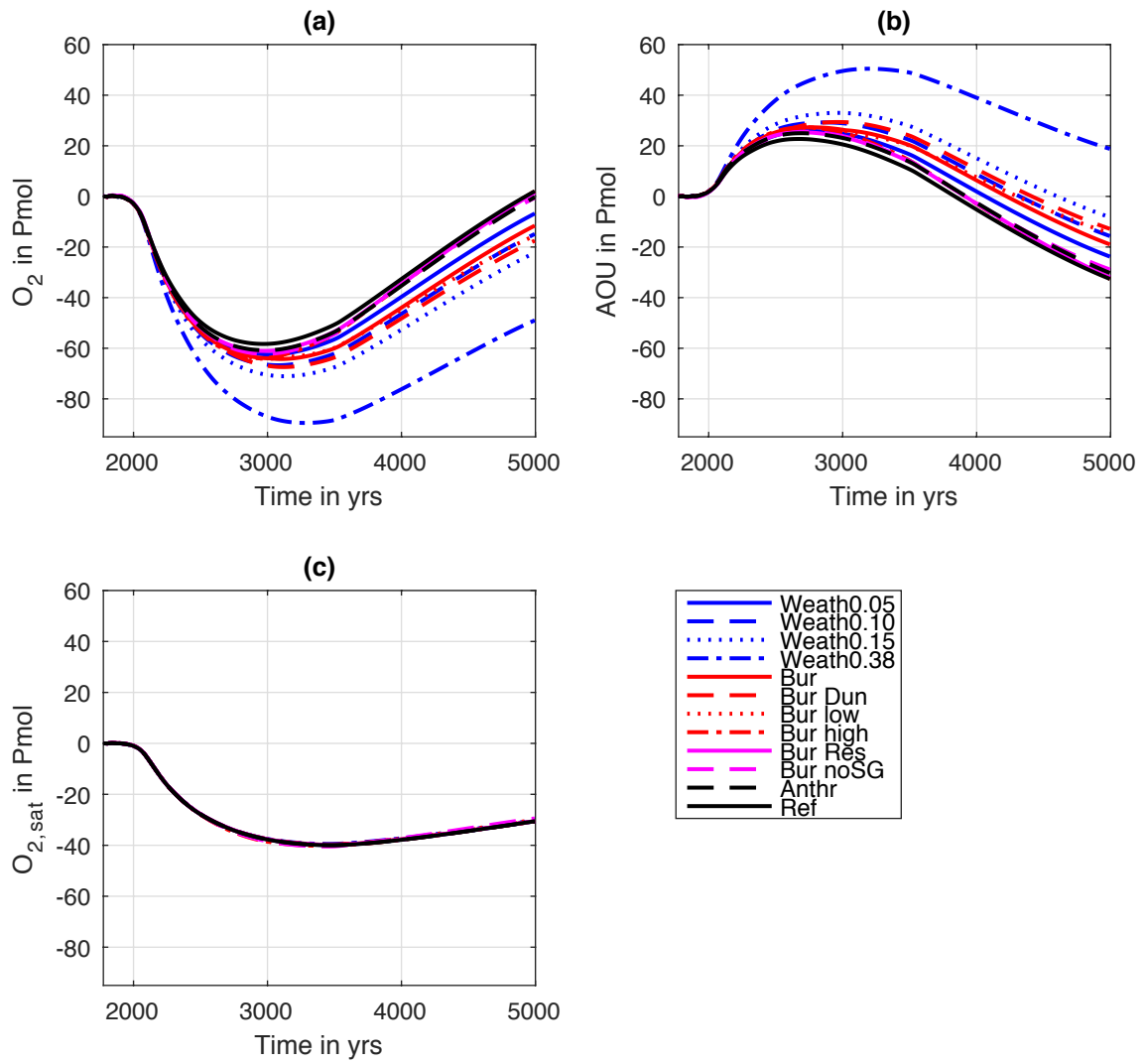
Fig. 9: Anomalies of globally integrated (a) O₂ content, (b) apparent oxygen utilization (AOU) and (c) oxygen saturation (O₂,sat) in Pmol O₂. Simulation descriptions can be found in Table 1.
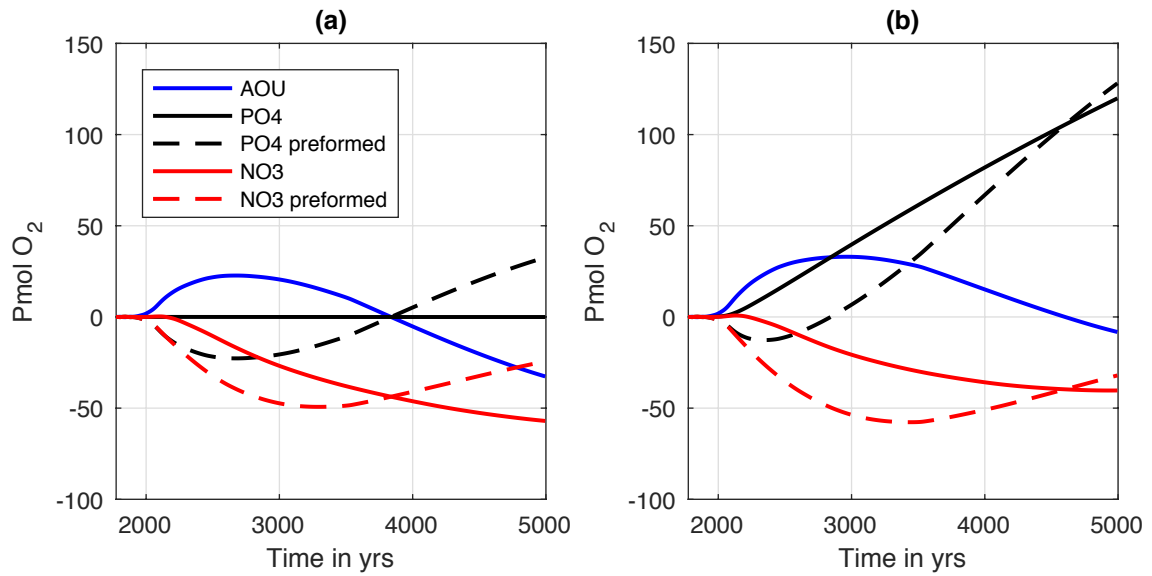
Fig. 10: Anomalies of globally integrated AOU (blue line), PO$_4$$^{3-}$ (black solid line), preformed PO$_4$$^{3-}$ (black dashed line), NO$_3$$^-$ (red solid line) and preformed NO$_3$$^-$ (red dashed line) expressed in Pmol O$_2$ equivalents using constant elemental ratios (O:N=10 and O:P=160) for the (a) *Ref* simulation and the (b) *Weath0.15* simulation. Preformed nutrients are calculated as the difference between remineralized and total nutrient content. The calculations assume that all ocean water leave the surface layer saturated in O$_2$.