

Phosphorus imbalance in the global ocean?

Klaus Wallmann

IFM-GEOMAR

Wischhofstrasse 1-3

24148 Kiel

Germany

email: kwallmann@ifm-geomar.de

Phone: 0049 431 600 2287

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Abstract

The phosphorus budget of the pre-human modern ocean is constrained applying the most recent estimates of the natural riverine, eolian, and ice-rafted input fluxes, the phosphorus burial in marine sediments, and the hydrothermal removal of dissolved phosphate from the deep ocean. This review of current flux estimates indicates that the phosphorus budget of the ocean is unbalanced since the accumulation of phosphorus in marine sediments and altered oceanic crust exceeds the continental input of particulate and dissolved phosphorus. The phosphorus mass balance is further tested considering the dissolved phosphate distribution in the deep water column, the marine export production of particulate organic matter, rain rates of phosphorus to the seafloor, benthic dissolved phosphate fluxes, and the organic carbon to phosphorus ratios in marine particles. These independent data confirm that the phosphate and phosphorus budgets were not at steady-state in the pre-human global ocean. The ocean is losing dissolved phosphate at a rate of $\geq 11.6 \times 10^{10} \text{ mol yr}^{-1}$ corresponding to a decline in the phosphate inventory of $\geq 4.5 \% \text{ kyr}^{-1}$. Benthic data show that phosphate is preferentially retained in pelagic deep-sea sediments where extended oxygen exposure times favor the degradation of particulate organic matter and the up-take of phosphate in manganese and iron oxides and hydroxides. Enhanced C : P regeneration ratios observed in the deep water column (>400 m water depth) probably reflect the preferential burial of phosphorus in pelagic sediments. Excess phosphate is released from continental margin sediments deposited in low-oxygen environments. The dissolved oxygen threshold value for the enhanced release of dissolved phosphate is $\sim 20 \mu\text{M}$. Benthic phosphate fluxes increase drastically when oxygen concentrations fall below this value.

1. Introduction

Phosphorus is the limiting nutrient in the oceans on geological time scales. The total inventory of phosphorus in the oceans is regulated by continental inputs and the burial flux at the seafloor. The phosphorus balance of the pre-human ocean is, however, poorly defined. Biogeochemical ocean models presume a constant global inventory of dissolved phosphate (NAJJAR et al., 2007) while some geochemical studies suggest an expansion of the phosphate inventory under glacial conditions and a corresponding phosphate decline during interglacials (BROECKER, 1982; TAMBURINI and FÖLLMI, 2009; WALLMANN, 2003).

The first comprehensive review of global marine phosphorus cycling was presented by FROELICH et al. (1982). At that time, the authors simply assumed that the long-term budget of dissolved phosphate in the oceans is at steady state since the input and output fluxes were poorly constrained. Their evaluation showed that most of the dissolved phosphate is delivered to the oceans via rivers and is removed from the seawater by the deposition of P-bearing margin and deep-sea sediments. The formation of phosphorites and the burial of fish debris were also investigated and shown to be of only minor importance (FROELICH et al., 1982). The residence time of dissolved phosphate in the global ocean was estimated as 80 000 years (FROELICH et al., 1982). Subsequently, the estimates for P-burial in marine sediments were refined applying new sequential extraction procedure allowing for a separation of reactive and refractory sedimentary P-phases (RUTTENBERG, 1992). The burial of reactive, potentially bio-available P occurs mainly at the continental margins. The global burial rate of reactive P was estimated as $8.0 - 18.5 \times 10^{10} \text{ mol yr}^{-1}$ applying up-dated estimates of global sediment burial at the seafloor and new reactive P concentration data (RUTTENBERG, 1993). The corresponding steady state residence time of dissolved phosphate in the global ocean was calculated to be only 16 000 – 38 000 years assuming that most of the deposited reactive P has been recycled through the marine biosphere (RUTTENBERG, 1993). RUTTENBERG (1993) also proposed that the phosphate inventory of the glacial ocean was enhanced due to the reduced burial of reactive P in shelf sediments during glacial sea-level low-stands. Additional studies on marine P cycling and burial in marine sediments were focused on

the burial of total P at the seafloor (FILIPPELLI, 1997), reactive P burial fluxes (DELANEY, 1998), and particulate organic P to organic C ratios in marine sediments (ANDERSON et al., 2001; INGALL and VAN CAPPELLEN, 1990). More recent reviews on the marine phosphorus turnover were mainly focused on the phosphorus cycling in the water column (BENITZ-NELSON, 2000; PAYTAN and MCCLAUGHLIN, 2007). Other studies tried to constrain potential changes in the dissolved phosphate inventory of the global ocean through geological time (FILIPPELLI and DELANEY, 1994; FÖLLMI, 1996; FÖLLMI et al., 1993; TSANDEV and SLOMP, 2009; TSANDEV et al., 2008; VAN CAPPELLEN and INGALL, 1994; WALLMANN, 2003). A recent study on the uptake of dissolved phosphate in oceanic crust via fluid flow through ridge flanks concluded that the modern phosphorus budget is unbalanced with total sinks outpacing sources (WHEAT et al., 2003). The budget of dissolved phosphate in the Holocene ocean was, however, never fully resolved in previous studies. It is, thus, unclear whether the oceanic inventory of dissolved phosphate is declining over the Holocene or maintained at a steady state level by balanced input and output fluxes.

The present contribution is constraining the pre-anthropogenic phosphorus sources and sinks drawing on new global flux data and a detailed evaluation of dissolved phosphate fluxes from surface sediments into the overlying bottom water. In the following, I will first (section 2) constrain the input and output fluxes determining the phosphorus inventory of the modern ocean applying recently published flux estimates (BATURIN, 2007; BEUSEN et al., 2005; HARRISON et al., 2005; MAHOWALD et al., 2008; RAISWELL et al., 2006; SEITZINGER et al., 2005; SYVITSKI et al., 2005; WHEAT et al., 1996; WHEAT et al., 2003). This mass balance is then tested and expanded considering the organic carbon and phosphate turnover at continental margins, the carbon and phosphate cycling in open ocean waters, the rain rates of particulate organic matter and phosphorus to the seafloor, and the dissolved phosphate fluxes across the sediment-water interface (section 3). The available evidence strongly suggests that the phosphate and phosphorus budgets were not at steady-state in the pre-human global ocean (section 4).

2. The phosphorus budget of the pre-human modern ocean

The inventory of dissolved phosphate in the ocean is regulated by continental inputs, the burial of phosphorus at the seafloor and hydrothermal processes removing dissolved phosphate from the oceans.

2.1 Phosphorus fluxes to the ocean

The natural riverine input of dissolved and particulate phosphorus into the ocean is poorly constrained because of the limited data base and the strong anthropogenic overprinting of the natural background fluxes. The natural flux of dissolved inorganic phosphorus (DIP) into the ocean is mainly driven by the weathering of apatite and has been estimated as $1.2 \times 10^{10} \text{ mol y r}^{-1}$ using the Global Nutrient Export from Watersheds (NEWS) model (HARRISON et al., 2005). The natural flux of dissolved organic phosphorus (DOP) amounts to $1.8 \times 10^{10} \text{ mol yr}^{-1}$ (SEITZINGER et al., 2005) contributing more than 50 % to the total dissolved P input ($3.0 \times 10^{10} \text{ mol yr}^{-1}$). Most of the riverine P input to the ocean is, however, associated with suspended particles. BEUSEN et al. (2005) estimate that $19 \times 10^{15} \text{ g yr}^{-1}$ of suspended particulate matter reached the oceans before the damming of river systems resulting in a particulate phosphorus flux of $32 \times 10^{10} \text{ mol yr}^{-1}$. The mean P content of river particles calculated from these numbers is $17 \text{ } \mu\text{mol P g}^{-1}$. The P concentration in riverine particles is thus close to the mean P level in continental crustal rocks previously estimated as $18 \text{ } \mu\text{mol g}^{-1}$ (FAURE, 1998). It should, however, be noted that continental erosion has been greatly accelerated by agriculture. Considering the effects of human land-use, the pre-anthropogenic flux of riverine particles into the oceans has been estimated as only $14 \times 10^{15} \text{ g yr}^{-1}$ (SYVITSKI et al., 2005). The pre-anthropogenic flux of riverine particulate P, thus, results as $24 \times 10^{10} \text{ mol yr}^{-1}$ applying the mean particle concentration of $17 \text{ } \mu\text{mol P g}^{-1}$ and the pre-anthropogenic particle flux given by SYVITSKI et al. (2005).

Additional particulate P is transported to the oceans by eolian dust and ice-rafted material. The pre-anthropogenic depositional flux of eolian phosphorus has recently been estimated as $1.7 \times 10^{10} \text{ mol yr}^{-1}$ (MAHOWALD et al., 2008). More than 80 % of the total eolian input is derived from mineral dust particles. Approximately 10 % of the eolian P is

released in the water column while the remaining 90 % are deposited at the seafloor. The mean P concentration in mineral dust is $\sim 23 \mu\text{mol g}^{-1}$ and the dust mass flux is $\sim 0.74 \times 10^{15} \text{ g yr}^{-1}$ (MAHOWALD et al., 2008). The mass flux of ice-rafted particles has been determined as $2.9 \times 10^{15} \text{ g yr}^{-1}$ (RAISWELL et al., 2006) while the mean P content of ice-rafted particles is currently unknown. The associated P flux may, however, be estimated as $5 \times 10^{10} \text{ mol yr}^{-1}$ applying the mean P level in continental crustal rocks ($18 \mu\text{mol g}^{-1}$; FAURE, 1998) and the mass flux estimated by RAISWELL et al. (2006).

The natural flux of dissolved phosphate via groundwater discharge into the ocean is much smaller than the riverine flux and probably insignificant at the global scale (SLOMP and VAN CAPPELLEN, 2004). It is thus not considered in the pre-anthropogenic phosphorus budget (Tab. 1).

Tab. 1. Modern pre-anthropogenic fluxes of phosphorus into the ocean

	Mass flux ($10^{15} \text{ g yr}^{-1}$)	Mean P concentration ($\mu\text{mol g}^{-1}$)	P flux ($10^{10} \text{ mol yr}^{-1}$)
Riverine dissolved P	-	-	3.0
Riverine particulate P	14	17	24
Eolian particulate P	0.74	23	1.7
Ice-rafted particulate P	2.9	18	5.0
Total	17.64		33.7

2.2 Phosphorus deposition at the seafloor

The global distribution of total particulate phosphorus in marine surface sediments was presented by BATURIN (1988), BATURIN and SAVENKO (1997), and BATURIN (2007). Each of the mean values listed in Tab. 2 is based on data retrieved at >100 stations by Russian scientists during Soviet time. According to these data, the mean P contents of terrigenous sediments deposited at the continental margins ($22.6 \mu\text{mol g}^{-1}$) are somewhat higher than the mean P level in continental crustal rocks ($\sim 18 \mu\text{mol g}^{-1}$; FAURE, 1998) while P is highly enriched in red clays and close to the mean crustal value in calcareous and siliceous pelagic sediments.

Tab. 2. Burial flux of phosphorus at the modern sea floor (BATURIN, 2007)

Sediment type	Mass flux (10^{15} g yr ⁻¹)	Mean P concentration ($\mu\text{mol g}^{-1}$)	P flux (10^{10} mol yr ⁻¹)
Shelf and slope	13.575	22.6	31
Hemipelagic	1.236	21.0	2.6
Calcareous pelagic	3.435	17.8	6.1
Siliceous pelagic	0.217	19.4	0.4
Red clays	0.331	48.4	1.6
Volcanogenic	0.048	37.1	0.2
Total	18.843	22.3	41.9

Phosphorus is also removed from the oceans by hydrothermal activity. Phosphate dissolved in the deep ocean is adsorbed on hydrothermal plume particles suspended in the water column and is bound in altered oceanic crust during hydrothermal circulation of seawater through ridge flanks (WHEAT et al., 1996; WHEAT et al., 2003). Phosphate adsorption on plume particles removes 0.8×10^{10} mol yr⁻¹ (WHEAT et al., 1996) while an additional removal flux of 2.8×10^{10} mol yr⁻¹ is induced by the uptake of seawater phosphate into altered crust during ridge-flank circulation (WHEAT et al., 2003). The total hydrothermal removal flux (3.6×10^{10} mol yr⁻¹) is thus higher than the riverine flux of dissolved phosphorus into the ocean (3.0×10^{10} mol yr⁻¹).

2.3 Mass balance of phosphorus in the modern ocean

The available data indicate that the total removal of phosphorus (45.5×10^{10} mol yr⁻¹) via hydrothermal activity (3.6×10^{10} mol yr⁻¹) and burial at the seafloor (41.9×10^{10} mol yr⁻¹, Tab. 2) is higher than the modern pre-anthropogenic phosphorus input to the global ocean (33.7×10^{10} mol yr⁻¹, Tab. 1). The modern flux imbalance results as 11.8×10^{10} mol yr⁻¹ or 35 % of the input flux (Fig. 1). The mass fluxes of particles (particle input from the continents: 17.64×10^{15} g yr⁻¹, sedimentation: 18.843×10^{15} g yr⁻¹) are rather well balanced. It should, however, be considered that most of the particles accumulating in the

pelagic carbonate and siliceous sediments are not derived from the continents but from marine biota. The CaCO_3 burial flux at the continental shelf ($1.0 \times 10^{15} \text{ g yr}^{-1}$; KLEYPAS, 1997), the accumulation of pelagic carbonates at the deep-sea floor ($1.0 \times 10^{15} \text{ g yr}^{-1}$; ARCHER, 1996), and the burial of biogenic opal at the seafloor ($0.27 \times 10^{15} \text{ g yr}^{-1}$; SARMIENTO and GRUBER, 2006) contribute significantly to the total sedimentation. Considering the accumulation of these biogenic components ($2.27 \times 10^{15} \text{ g yr}^{-1}$) and the continental particle export ($17.64 \times 10^{15} \text{ g yr}^{-1}$, Tab. 1), the total sedimentation rate at the seafloor should be $19.91 \times 10^{15} \text{ g yr}^{-1}$. The number given in Tab. 2 is smaller ($18.843 \times 10^{15} \text{ g yr}^{-1}$) and hence the excess P burial indicated by the phosphorus mass balance is not caused by an overestimation of the total sedimentation rate at the seafloor.

By far the largest fluxes of phosphorus are associated with the input of riverine particles and the sedimentation of terrigenous sediments at the continental slope and rise (Fig. 1). These fluxes are not well constrained such that the apparent imbalance in the phosphorus budget might not be significant. In the following section, I will, thus, discuss independent data and flux estimates to further constrain the phosphorus mass balance. These include the phosphate distribution in the water column, the marine export production of particulate organic matter, rain rates of phosphorus to the seafloor, benthic dissolved phosphate fluxes, and the organic carbon to total phosphorus ratios in marine particles.

3 Phosphorus cycling in the global ocean

3. 1 Phosphorus binding forms and turnover in the coastal zone

Particulate phosphorus occurs in various binding forms. An unequivocal separation of P-binding forms is not feasible with the existing analytical techniques. The P fractions are, thus, operationally defined through sequential leaching steps (RUTTENBERG, 1992). P is basically separated into residual and reactive phosphorus using the SEDEX and similar procedures (RUTTENBERG and BERNER, 1993). Reactive P (PR) includes any kind of P that was at some point part of the biomass in the terrestrial or marine environment. The corresponding reactive solid P phases are: P associated with organic matter, labile P reversely adsorbed to surfaces, oxide-associated P, P in authigenic carbonate fluorapatite minerals (CFA), and P in fish bone. Residual P is apatite of igneous and metamorphic

origin being delivered to the oceans in particulate form via continental erosion. Igneous and metamorphic apatite occurs as coarse (>2 mm) crystals and is a common heavy mineral in the sand and silt fraction (BERNER et al., 1993). Detrital P is thus a major portion of the total particulate P pool only at sites where coarse grained material is being transported and deposited.

The concentration and speciation of P in riverine suspended particles were determined by (BERNER and RAO, 1994) at the lower Amazon River. The total particulate P concentration (P) was $20.9 \pm 0.7 \mu\text{mol/g}$ and the mean reactive P content (PR) was $17.7 \pm 0.7 \mu\text{mol/g}$. Riverine suspended particles were also analyzed at the lower Mississippi River (SUTULA et al., 2004). The particles were enriched in phosphorus ($P = 35 \mu\text{mol g}^{-1}$) and 98 % of the P occurred in reactive form. Both studies show that most of the phosphorus in riverine particles is reactive. The reactive phosphorus is ultimately derived from continental apatite weathering. The dissolved phosphate released during this weathering process is taken-up by plants and cycled through the terrestrial biosphere. It is finally transformed into reactive solid phases in the soil and fresh water environments.

The Amazon and Mississippi River studies showed that terrigenous sediments deposited at the continental shelf, close to the river mouths, are depleted in phosphorus with respect to the corresponding riverine particles entering the coastal zone (BERNER and RAO, 1994; SUTULA et al., 2004). The decrease in particulate phosphorus is probably caused by the release of dissolved phosphate into coastal waters. Some of the phosphate is displaced from particles during their passage through the estuary by seawater ions adsorbing to the particle surfaces. Most of the phosphate is, however, released from reducing coastal sediments where reactive phosphorus phases are degraded and dissolved by anaerobic organic matter decomposition (SUTULA et al., 2004). The Amazon and Mississippi River studies imply that 22 – 48 % of the riverine particle-bound phosphorus entering the oceans might be released as dissolved phosphate into coastal waters (SUTULA et al., 2004).

Global mean phosphorus concentrations listed in Tab. 1 and 2 are apparently not consistent with this concept since the P value in shelf and slope sediments ($22.6 \mu\text{mol g}^{-1}$;

(BATURIN, 2007) is higher than the P concentration in riverine particles ($17 \mu\text{mol g}^{-1}$; (BEUSEN et al., 2005). The mean sediment value is, however, not representative for the river mouth regions but is covering the much broader area of the continental shelf and slope. Shelf and slope sediments receive phosphorus from marine particles sinking to the seafloor and a significant portion of the marine particulate P is buried in these deposits. It thus seems that terrigenous particles are initially depleted in P during their passage through the estuary and the coastal zone to be subsequently reloaded with marine phosphorus in the continental shelf and slope environment.

3.2 Phosphorus cycling at continental margins

A large fraction of the marine primary production and export production takes place at the continental margins. Ocean biogeochemical models predict that the continental margins may account for up to 44 % of the global export production even though they cover only ~10 % of the world ocean (GIRAUD et al., 2008). The export production of marine particulate organic phosphorus (POP) at the continental margins was estimated as $200 - 400 \times 10^{10} \text{ mol yr}^{-1}$ (DUNNE et al., 2007; GIRAUD et al., 2008). The flux of marine POP to the seafloor (0 – 2000 m water depth) may be as high as $140 \times 10^{10} \text{ mol yr}^{-1}$ (DUNNE et al., 2007).

A large fraction of the particulate phosphorus being deposited at the margin seafloor is degraded in surface sediments and transformed into dissolved phosphate. The dissolved phosphate accumulating in sediment pore waters is partly recycled into the overlying bottom water via molecular diffusion and bio-irrigation. The remaining fraction is retained in the sediments by adsorption on sediment surfaces and the precipitation of authigenic phosphorus-bearing minerals. Benthic chambers were deployed at a number of continental margin sites to measure the total benthic flux of dissolved phosphate from sediments into the bottom water. These high-quality in-situ flux measurements were performed at the continental margins of Northwest Mexico (HARTNETT and DEVOL, 2003), Washington State (DEVOL and CHRISTENSEN, 1993; HARTNETT and DEVOL, 2003), Central California (BERELSON et al., 1996; INGALL and JAHNKE, 1994; INGALL and JAHNKE, 1997; MCMANUS et al., 1997), the California borderland basins (BERELSON et

al., 1996; INGALL and JAHNKE, 1997; MCMANUS et al., 1997), and the eastern North Pacific (INGALL and JAHNKE, 1997). The degradation of particulate organic matter (POM) in marine surface sediments was also quantified at these sites using the benthic fluxes of oxygen into the sediment and additional data. Fig. 2 shows that the ratio between the depth-integrated rate of POC degradation and the benthic phosphate release (r_{REG}) is clearly a function of bottom water oxygenation in continental margin sediments.

Massive amounts of excess phosphate are released under low oxygen conditions ($<20 \mu\text{M}$) whereas the C : P regeneration ratios (r_{REG}) cluster around the Redfield value under normal oxygen conditions ($>20 \mu\text{M}$). The oxygen effect has been observed in a number of previous studies and is usually ascribed to the reductive dissolution of P-bearing manganese and iron oxides and hydroxides and the preferential degradation of POP in anoxic marine sediments (ALGEO and INGALL, 2007; INGALL et al., 1993; INGALL and JAHNKE, 1994; INGALL and JAHNKE, 1997; SLOMP et al., 2002; SLOMP et al., 2004; SLOMP and VAN CAPPELLEN, 2007; VAN CAPPELLEN and INGALL, 1994; VAN CAPPELLEN and INGALL, 1996; WALLMANN, 2003).

The following function was applied to describe the oxygen-dependence of the regeneration ratio (r_{REG}):

$$r_{\text{REG}} = \frac{\text{RPOC}}{\text{BenPO4}} = Y_{\text{F}} + A \cdot \exp\left(-\frac{\text{O}_2}{r}\right) \quad (1)$$

where RPOC is the depth-integrated rate of organic matter degradation in surface sediments and BenPO4 is the benthic flux of dissolved phosphate into the bottom water. The model parameters were determined as $Y_{\text{F}} = 123 \pm 24$, $A = -112 \pm 24$, and $r = 32 \pm 19$ applying a statistical weighting method (weights = $1/r_{\text{REG}}$). The fit (solid line in Fig. 2) indicates that the regeneration ratio under oxic conditions (Y_{F}) is probably higher than the Redfield value.

Eq. 1 can be used to predict sedimentary regeneration ratios for contrasting oxygen-conditions. In the modern ocean, less than 1 % of the total seafloor area at continental margins is covered by low oxygen waters ($<20 \mu\text{M}$). The contribution of these low-oxygen areas to the total benthic flux of dissolved phosphate is, thus, currently not significant. However, oxygen minimum zones have expanded significantly over the last decades (STRAMMA et al., 2008) and models predict a further expansion of oxygen minimum zones in response to anthropogenic CO_2 emissions and global warming (OSCHLIES et al., 2008). The release of excess phosphate from these low-oxygen environments may enhance marine productivity and oxygen respiration and could thereby amplify future oxygen change (VAN CAPPELLEN and INGALL, 1994; WALLMANN, 2003).

Since the regeneration of P from margin sediments shows near Redfield behavior under normal marine conditions, the benthic fluxes of dissolved phosphate into the overlying water column can be estimated from the depth-integrated rate of POC degradation in marine surface sediments deposited at the continental margins. This rate (RPOC) is defined by the following steady-state mass balance:

$$\text{RPOC} = \text{RRPOC} - \text{APOC} \quad (2)$$

where RRPOC is the rain rate of POC to the seafloor and APOC is the accumulation of POC below the bioturbated surface zone. The total POC accumulation rate in shelf and slope sediments has been estimated as $9.83 \text{ Tmol yr}^{-1}$ (BATURIN, 2007). An additional amount of $0.58 \text{ Tmol yr}^{-1}$ accumulates in hemipelagic sediments deposited at the continental rise (s. Tab. 3). A previous estimate based on sedimentary data yields a value of 12 Tmol yr^{-1} for the POC accumulation at continental margins (HEDGES and KEIL, 1995). The POC burial flux is, however, poorly constrained. A large range of values ($10 - 200 \text{ Tmol yr}^{-1}$) has been derived applying top-down approaches and bottom-up estimates (BURDIGE, 2007). In the top-down approach, estimates of marine export production are applied to constrain the POC burial flux while POC concentrations in sediments and bulk sedimentation rates are considered in the bottom-up approach. The bottom-up approach is probably more robust and yields lower values than the top-down

method. However, the sedimentary estimates of POC burial are impaired by the heterogeneity of shelf sediments. Approximately 70 % of the sediments deposited at the continental shelf are sandy containing very low amounts of POC whereas ~30 % are fine grained and strongly enriched in POC (BURDIGE, 2007). The estimate by BATURIN (2007) applied below is based on a very comprehensive data set considering, both, the low POC burial in sandy shelf deposits and the high burial rates in fine-grained sediments.

The rain rate of POC to the seafloor (RRPOC) can be estimated considering the burial efficiency of POC. The burial efficiency (BE in %) is defined as:

$$BE = \frac{A_{POC}}{RRPOC} \cdot 100 \quad (3)$$

It is known to depend on sedimentation rate, O₂ concentrations in ambient bottom waters, and the grain size of sediments (BURDIGE, 2007; CANFIELD, 1993). BE is very low in sandy shelf sediments (~1 %; BURDIGE, 2007) and high in muddy shelf deposits (~30 %; BURDIGE, 2007; CANFIELD, 1993). Applying a mean BE value of ~10 %, the rain rate for shelf and slope sediments results as RRPOC = 98 Tmol yr⁻¹. Applying the same BE value to the hemipelagic sediments deposited at the continental rise, the corresponding value results as RRPOC = 5.8 Tmol yr⁻¹. The total rain rate at the continental margins is thus 103.8 Tmol yr⁻¹. It should be considered that a significant fraction of the POC raining to the seafloor is derived from the continents. The mean atomic POC/P ratio in riverine suspended particles entering the oceans is 56 (SEITZINGER et al., 2005). Applying this ratio to the pre-anthropogenic mass flux of phosphorus bound in riverine, ice-rafted, and eolian particles (30.7 x 10¹⁰ mol yr⁻¹, Tab. 1), the pre-anthropogenic terrestrial POC flux to the ocean results as 17.2 Tmol yr⁻¹. The rain rate of marine POC to the margin seafloor is calculated by difference as 86.6 Tmol yr⁻¹.

This flux is significantly smaller than the POC rain rate to the margin seafloor (0 – 2000 m water depth) derived by ocean biogeochemical modeling (165 ± 64 Tmol yr⁻¹; (DUNNE et al., 2007). Ocean circulation and biogeochemical processes in the coastal zone and at

the continental shelves are, however, poorly resolved by these global ocean models (GIRAUD et al., 2008). It is also possible that a significant fraction of POC raining to the seafloor is re-suspended by strong bottom currents and degraded in the water column. The difference between the benthic bottom–up estimate and the top-down estimate derived from ocean modeling may, thus, be related to sediment re-suspension.

Using the benthic data and mass balance, the overall POC degradation rate in marine surface sediments deposited at the continental shelf, slope, and rise results as RPOC = 93.4 Tmol yr⁻¹ (Tab. 3 and Tab. 4). Previous estimates for RPOC in continental margin sediments range in between 40 and 230 Tmol yr⁻¹ (BURDIGE, 2007). The new RPOC value presented in this paper is thus consistent with previous estimates derived from benthic observations.

The ratio between organic carbon mineralization in continental margin sediments and the benthic release of dissolved phosphate (r_{REG}) is further constrained applying the following mass balance equation:

$$r_{\text{REG}} = \frac{\text{RRPOC} - \text{APOC}}{\text{RRP} - \text{AP}} \quad (4)$$

where AP is the accumulation rate of phosphorus in surface sediments. The rain rate of particulate P to the seafloor (RRP) includes a marine and a terrestrial component. The marine P flux is calculated as 81.7×10^{10} mol yr⁻¹ from the marine POC rain rate (86.6 Tmol yr⁻¹) and the Redfield ratio (106 : 1). Considering the terrestrial particulate P flux (30.7×10^{10} mol yr⁻¹, Tab. 1), the total rain of particulate P to the margin seafloor results as 112.4×10^{10} mol yr⁻¹. Most of the phosphorus being deposited at the continental margins, thus, originates from marine export production. Inserting the RRP value derived above, the accumulation rates listed in Tab. 2 and Tab. 3, and the POC rain rate (RRPOC = 103.8 Tmol yr⁻¹) into Eq. (4), yields an atomic r_{REG} value of 118. This value is higher than the Redfield ratio and consistent with the oxic flux ratio ($Y_{\text{F}} = 123 \pm 24$) derived from the independent benthic flux data (Fig. 1). The good match between r_{REG} and Y_{F}

confirms that the rain rates and accumulation rates applied in Eq. (4) are representative for the global continental margins.

Tab. 3. Particulate organic carbon turnover and benthic phosphate fluxes in marine surface sediments. Seafloor areas (Area), mean POC concentrations in surface sediments (POC), atomic POC/P ratios in surface sediments, and POC accumulation rates (APOC) are taken from BATURIN (2007). Depth-integrated rates of POC degradation in surface sediments (RPOC), atomic regeneration ratios (r_{REG}), and benthic phosphate fluxes (BenPO₄) are calculated as described in the text. RPOC and BenPO₄ values for the individual pelagic sediment types are estimated applying the total POC rain rate to pelagic deep-sea sediments (38 Tmol yr⁻¹; SEITER et al., 2005) and the corresponding depositional areas for each sediment type.

Sediment type	Area (10⁶ km²)	POC (wt-%)	POC/P (atomic)	APOC (Tmol yr⁻¹)	RPOC (Tmol yr⁻¹)	r_{REG}	BenPO₄ (10¹⁰ mol yr⁻¹)
Shelf and slope	90	0.87	32	9.83	88.2	118	75
Hemipelagic	20.6	0.57	23	0.58	5.2	118	4
Calcareous pelagic	114.5	0.38	18	1.09	16.3	140	12
Siliceous pelagic	43.3	0.30	13	0.06	6.5	140	5
Red clays	82.8	0.27	5	0.08	12.5	140	9
Volcanogenic	9.5	0.32	9	0.02	1.4	140	1
Total	361.2	0.74	28	11.67	130.1	123	106

Applying the phosphorus mass balance ($\text{BenPO}_4 = \text{RRP} - \text{AP}$), the total benthic flux of dissolved phosphate (BenPO_4) from shelf, slope, and rise sediments into the water column is finally calculated as $79 \times 10^{10} \text{ mol yr}^{-1}$. The individual contribution of shelf and slope sediments and hemipelagic sediments is calculated applying the r_{REG} value to the corresponding RPOC rates (s. Tab. 3). The benthic phosphate fluxes are calculated from a

mass balance assuming that the entire particulate P delivered from the continents ($30.7 \times 10^{10} \text{ mol yr}^{-1}$, Tab. 1) is deposited at the margin seafloor. Therefore, these fluxes include the release of dissolved phosphate from riverine particles in the coastal zone ($5 - 11 \times 10^{10} \text{ mol yr}^{-1}$; SUTULA et al., 2004) and the desorption of phosphate from eolian particles ($\sim 0.2 \times 10^{10} \text{ mol yr}^{-1}$; MAHOWALD et al., 2008).

Overall, the phosphorus turnover at continental margins is remarkably well balanced. The total burial of phosphorus ($33.6 \times 10^{10} \text{ mol yr}^{-1}$) is as high as the continental input of dissolved and particulate P ($33.7 \times 10^{10} \text{ mol yr}^{-1}$). The C : P regeneration ratio in sediments is higher than the C : P ratio in marine plankton sinking to the seafloor. From a mass balance perspective, the enhanced phosphorus burial compensates for the riverine input of dissolved phosphorus and the dissolved phosphate release from riverine particles in the coastal zone. The margins are thus effectively removing the entire continental phosphorus input to the global ocean.

Tab. 4. Global fluxes of particulate organic carbon (in Tmol yr^{-1}) at continental margins and in open oceans considered in the phosphorus mass balance. Export production values (EXPOC) are taken from DUNNE et al. (2007). The export production through the 400 m depth horizon (EXPOC400) is calculated from EXPOC applying the Martin relation. Rain rates of POC (RRPOC) to margin sediments are derived from POC accumulation rates and burial efficiencies whereas the rain rate to pelagic deep-sea sediments is taken from SEITER et al. (2005). POC accumulation rates (APOC) are from BATURIN (2007) and depth-integrated rates of POC degradation in surface sediments (RPOC) are calculated applying Eq. (2).

	Continental margin	Open ocean
EXPOC	250 ± 90	546 ± 212
EXPOC400	-	175 (90 – 300)
RRPOC	103.8	38
RPOC	93.4	36.7
APOC	10.4	1.25

It should be noted that the phosphorus fluxes at the continental margins derived above are based on very conservative estimates of the POC rain rate to the margin seafloor and the POC burial flux (Tab. 4) when compared to results from global ocean modeling (DUNNE et al., 2007). The benthic phosphate flux and the phosphorus burial flux would result as $\text{BenPO}_4 = 82 \times 10^{10} \text{ mol yr}^{-1}$ and $\text{AP} = 104 \times 10^{10} \text{ mol yr}^{-1}$, respectively, applying the estimates derived from ocean modeling ($\text{RRPOC} = 165 \text{ Tmol yr}^{-1}$; $\text{APOC} = 64 \text{ Tmol yr}^{-1}$; DUNNE et al., 2007), the benthic regeneration ratio constrained by benthic chamber deployments at the margin seafloor ($r_{\text{REG}} = 123$, Fig. 1), and the terrestrial input of particulate P to the ocean ($30.7 \times 10^{10} \text{ mol yr}^{-1}$, Tab. 1). While, the benthic phosphate flux is close to the estimate derived above, the burial flux of P is enhanced by a factor of ~ 3 . With this estimate, the margins would serve as a net phosphorus sink and the burial flux at the margins would be ~ 3 times higher than the continental phosphorus input to the ocean. Independent biogeochemical ocean models, thus, indicate that the phosphorus loss to sediments is much higher than the terrestrial phosphorus input to the global ocean. Their results imply a strong imbalance in the global marine phosphorus balance.

3.3 Particulate organic carbon and phosphorus cycling in the open ocean

The export production of POC into the deep ocean, the rain rate of POC to the deep-sea floor ($>2000 \text{ m}$ water depth), and the burial of POC in hemipelagic and pelagic sediments have been estimated as $546 \pm 212 \text{ Tmol yr}^{-1}$, $26 \pm 25 \text{ Tmol yr}^{-1}$, and $1.0 \pm 1.7 \text{ Tmol yr}^{-1}$, respectively, by biogeochemical ocean modeling (DUNNE et al., 2007). The evaluation of benthic oxygen fluxes suggests a POC rain of $\sim 42 \text{ Tmol yr}^{-1}$ to the deep-sea floor ($>1000 \text{ m}$ water depth; (SEITER et al., 2005) while sedimentary data show that $1.83 \text{ Tmol yr}^{-1}$ of POC are buried in hemipelagic and pelagic sediments (BATURIN, 2007), Tab. 3). Top-down model results and bottom-up benthic data are, thus, broadly consistent for the open ocean and the deep-sea floor (Tab. 4).

The mean atomic ratio between organic carbon and phosphorus in marine biomass is 106 : 1 (REDFIELD, 1958; SARMIENTO and GRUBER, 2006). However, the analysis of nutrient distributions in the deep ocean ($>400 \text{ m}$ water depth) implies that dissolved inorganic carbon and phosphate are released at a significantly higher ratio (C : P = 117 : 1) by the

degradation of organic matter in the ocean's interior (ANDERSON and SARMIENTO, 1994; SARMIENTO and GRUBER, 2006). Moreover, the hydrogen, oxygen, and phosphorus contents of particulate marine organic matter imply that 150 mol of oxygen are consumed to release 1 mol of dissolved phosphate whereas the dissolved oxygen and phosphate ratios in the deep ocean suggest a significantly higher oxygen consumption of 170 mol O₂ per mol of phosphate (SARMIENTO and GRUBER, 2006). From a benthic perspective, these conflicting observations suggest that the POC/P burial ratio in deep-sea sediments may be much lower than the Redfield value. Phosphorus may be preferentially retained in pelagic sediments such that the return flux of dissolved phosphate into the ocean is significantly smaller than predicted by the Redfield ratio.

A simple mass balance is set-up to control this hypothesis. The C/P regeneration ratio observed in the water column data ($r_{REG} = 117$) is related to the POC export production at 400 m water depth (EXPOC400) and the POC burial rate (APOC = 1.83 Tmol yr⁻¹) as:

$$r_{REG} = \frac{EXPOC400 - APOC}{EXPOC400 / r_{EX} - APOC / r_B} \quad (5)$$

where r_{EX} is the C : P ratio of organic matter exported to >400 m water depth (~106) and r_B the POC/P burial ratio. EXPOC400 is estimated as 90 - 300 Tmol yr⁻¹ from the export production at 100 m water depth (EXPOC = 546 ± 212 Tmol yr⁻¹) applying the Martin equation (EXPOC400/EXPOC = (400/100)^{-b}); MARTIN et al., 1987) with b = 0.82 ± 0.16 (BERELSON, 2001).

Solving for r_B :

$$r_B = \frac{APOC \cdot r_{EX} \cdot r_{REG}}{APOC \cdot r_{EX} + EXPOC400 \cdot (r_{REG} - r_{EX})} \quad (6)$$

and inserting the values given above, results in $r_B = 6 - 20$.

Sedimentary data (BATURIN, 2007) indeed show that the POC/P burial ratio (r_B) is significantly reduced in pelagic sediments (Tab. 3). The POC/P burial ratio in pelagic sediments ($r_B = 5 - 18$) complies with the range of values predicted by the mass balance ($r_B = 6 - 20$). It is, thus, very likely that the regeneration of phosphate in the deep ocean is indeed diminished by the enhanced burial of phosphorus in pelagic sediments.

In Eq. (6), Redfield stoichiometry is assumed for the particles sinking into the deep ocean ($r_{EX} = 106$). The POC/P ratio of these particles is, however, poorly constrained. FAUL et al. (2005) analyzed reactive phosphorus phases in particles sinking through the water column in a wide range of oceanic regimes. The mean molar ratio between POC and total P in particles caught in sediment traps at >300 m water depth ($r_{EX} \approx 175$) was significantly higher than the Redfield value. FAUL et al. (2005), thus, concluded that organic phosphorus is preferentially degraded within the upper water column.

In the deeper water column (>300 m), the POC/P ratio was approximately constant implying near Redfield behavior. However, ANTIA (2005) demonstrated that significant fractions of elements bound in sinking particles, once caught in sediment trap jars, are released into the dissolved phase. The composition of dissolved elements analyzed in trap jar supernatant showed that particulate phosphorus phases collected in the sediment trap jars are more soluble than C and N phases. The atomic N : P and C : P ratios in the particulate phase are, thus, systematically overestimated when the contribution by dissolved elements is not considered in the evaluation. Taking account for the fraction dissolved in the trap jar, the N : P ratios were found to be close to the Redfield value for mid-water traps at the European continental margin (580 and 600 m water depth).

The mass balance above can be used to constrain the poorly defined POC/P ratio in particles sinking into the deep ocean through the 400 m water depth horizon. The mean POC/P burial ratio in hemipelagic and pelagic sediments is $r_B = 16.8$ (BATURIN, 2007) while the best estimate for the export production of POC at 400 water depth is calculated as $EXPOC_{400} = 175 \text{ Tmol yr}^{-1}$ applying the Martin relation with $b = 0.82$ and $EXPOC = 546 \text{ Tmol yr}^{-1}$. Solving Eq. (6) for r_{EX} :

$$r_{EX} = \frac{EXPOC400 \cdot r_B \cdot r_{REG}}{EXPOC400 \cdot r_B + APOC \cdot (r_{REG} - r_B)} \quad (7)$$

and inserting the values given above results in $r_{EX} = 110$. The POC/P ratio in particles sinking into the deep ocean is, thus, probably higher than the Redfield value and lower than the regeneration ratio in the deep ocean.

The ratio between organic carbon mineralization in pelagic sediments and the benthic release of dissolved phosphate (r_{REG}) is estimated applying the following mass balance equation:

$$r_{REG} = \frac{RRPOC - APOC}{\frac{RRPOC}{r_{EX}} - \frac{APOC}{r_B}} \quad (8)$$

The rain rate of POC to the deep-sea floor (excluding the continental margin provinces) is $RRPOC = 38 \text{ Tmol yr}^{-1}$ (SEITER et al., 2005) while the POC accumulation in pelagic sediments (excluding the hemipelagic deposits) is $APOC = 1.25 \text{ Tmol yr}^{-1}$ (BATURIN, 2007). The corresponding POC/P burial ratio in pelagic sediments is $r_B = 15.1$ (BATURIN, 2007) whereas the POC/P ratio in particles sinking to the seafloor is $r_{EX} = 110$. Inserting these values into Eq. (8), yields a regeneration ratio in pelagic sediments of $r_{REG} = 140$.

Benthic fluxes of dissolved phosphate at the deep-sea floor were determined by a benthic chamber deployment in the eastern North Pacific (SMITH JR. et al., 1979). The regeneration ratio determined in this deployment was 158 confirming that phosphorus is preferentially retained in deep-sea sediments (INGALL and JAHNKE, 1997; SMITH JR. et al., 1979). Moreover, diffusive phosphate fluxes into the overlying bottom water were calculated from gradients of dissolved phosphate across the sediment-water interface at a large number of deep-sea sites (COLMAN and HOLLAND, 2000; ZABEL et al., 1998). The diffusive benthic fluxes in the eastern South Atlantic were usually much smaller than predicted by the Redfield value (ZABEL et al., 1998). The mean diffusive flux of dissolved phosphate from pelagic sediments was $0.7 \pm 1.8 \text{ mmol m}^{-2} \text{ a}^{-1}$ (ZABEL et al.,

1998). Considering the mean sedimentary POC degradation rate in this area ($\sim 120 \text{ mmol m}^{-2} \text{ a}^{-1}$; SEITER et al., 2005), the regeneration ratio results as ~ 170 . HENSEN et al. (1998) reported benthic phosphate fluxes for the entire South Atlantic. The fluxes were $\leq 0.25 \text{ mmol m}^{-2} \text{ a}^{-1}$ in low-productivity areas of the central South Atlantic. Carbon and phosphate are apparently regenerated at very high C/P ratios in these slowly accumulating pelagic sediments ($r_{\text{REG}} > 200$). Significantly higher phosphate fluxes and lower r_{REG} values were observed at the continental margins and in high-productivity areas of the South Atlantic (HENSEN et al. 1998). The global compilation of diffusive phosphate fluxes by COLMAN and HOLLAND (2000) indicates a mean dissolved phosphate flux of $0.7 \pm 0.9 \text{ mmol m}^{-2} \text{ a}^{-1}$ from sediments deposited at $>1000 \text{ m}$ water depth. Applying the mean sedimentary POC degradation rate at $>1000 \text{ m}$ water depth ($140 \text{ mmol m}^{-2} \text{ yr}^{-1}$; SEITER et al., 2005), the regeneration ratio results as ~ 200 . It should, however, be considered that the total phosphorus fluxes from sediments may be higher than the diffusive fluxes calculated from pore water gradients since bio-irrigation may contribute to the overall flux. The difference between the r_{REG} value derived from pore water data ($r_{\text{REG}} \sim 200$) and the mass balance ($r_{\text{REG}} = 140$) may be related to this effect. However, the available data on benthic phosphate fluxes at the deep-sea floor confirm that phosphorus is preferentially retained in pelagic sediments. From a benthic perspective, the phosphorus turnover in the global ocean is clearly not governed by the classical Redfield ratio (Fig. 3).

Pelagic surface sediments are exposed to high oxygen concentrations over extended periods of time because of low sedimentation and oxygen consumption rates. The degradation of organic matter is promoted by these extended oxygen exposure times (HEDGES et al., 1999; MEILE and CAPPELLEN, 2005) whereas the oxic conditions favor the retention of phosphorus in sediments via adsorption on iron and manganese oxides and hydroxides (COLMAN and HOLLAND, 2000). The phosphate deficit in the deep water column is, thus, caused by the opposing response of sedimentary organic carbon and phosphorus to enhanced oxygen exposure.

The phosphorus fluxes in the open ocean are not balanced since the continental input flux is almost entirely removed at the continental margins. Eolian transport is the only pathway for particulate phosphorus to the open ocean. Even if the entire dust flux would be deposited in the open ocean, the eolian phosphorus input ($1.7 \times 10^{10} \text{ yr}^{-1}$; MAHOWALD et al., 2008) could not compensate for the removal flux via burial in pelagic sediments ($8.3 \times 10^{10} \text{ yr}^{-1}$) and the dissolved phosphate uptake in hydrothermal plume particles and oceanic crust ($3.6 \times 10^{10} \text{ mol yr}^{-1}$). The deep-sea floor thus serves as phosphorus sink contributing significantly to the imbalance in the oceanic phosphorus cycle.

3. 4 Dissolved phosphate budget of the global ocean

The input of dissolved phosphate to the global oceans is clearly dominated by the benthic turnover in marine surface sediments. The total benthic release of dissolved phosphate from marine sediments ($106 \times 10^{10} \text{ mol yr}^{-1}$, Tab. 3) is much higher than the input of riverine dissolved phosphorus to the ocean ($3 \times 10^{10} \text{ mol yr}^{-1}$, Tab. 1). The benthic fluxes are dominated by the contribution of shelf and slope sediments (Tab. 3). These continental margin fluxes include the dissolved phosphate release from riverine and eolian particles. Considering the POC/P ratios in marine particles and their regeneration ratios, the total input of dissolved phosphorus into the ocean ($109 \times 10^{10} \text{ mol yr}^{-1}$, Tab. 5) is estimated to be smaller than the removal flux via deposition of marine organic matter at the seafloor and via hydrothermal activity ($120.6 \times 10^{10} \text{ mol yr}^{-1}$, Tab. 6). The resulting dissolved phosphate deficit ($11.6 \times 10^{10} \text{ mol yr}^{-1}$) corresponds to the phosphorus deficit estimated in section 2.3 ($11.6 \times 10^{10} \text{ mol yr}^{-1}$). It should again be considered that the rain rates of marine POP to the seafloor listed in Tab. 5 are conservative estimates being approximately two times lower than the corresponding removal fluxes derived from biogeochemical ocean modeling (DUNNE et al., 2007). Moreover, the benthic fluxes are based on conservative estimates of the regeneration ratio. Benthic chamber deployments (section 3.2, Fig. 1) and pore water gradients (section 3.3) indicate higher r_{REG} values for margin and deep-sea sediments corresponding to lower benthic phosphate fluxes. The imbalance in the phosphate budget may, thus, be higher than estimated in Tab. 5. Considering the available evidence, it is very likely that the phosphate and phosphorus budgets are not at steady-state in the pre-human global ocean.

Tab. 5. Dissolved phosphorus budget of the pre-human global ocean

	Flux (10^{10} mol yr ⁻¹)
Sources	
Riverine dissolved P	3
Benthic flux from continental margin sediments	79
Benthic flux from pelagic deep-sea sediments	27
Total	109
Sinks	
Rain rate of marine POP to the margin seafloor	82
Rain rate of marine POP to the deep-sea floor	35
Hydrothermal removal of dissolved phosphate	3.6
Total	120.6

The turnover of dissolved organic phosphorus (DOP) in the ocean is considered implicitly in the mass balance. It is assumed that the riverine DOP (SEITZINGER et al., 2005) and the marine DOP formed in the upper ocean (PAYTAN and MCLAUGHLIN, 2007) are ultimately converted into dissolved phosphate or buried in the sediment.

The residence time of dissolved phosphate in the global ocean is calculated as only 2 kyr considering the modern inventory of dissolved phosphate in the global ocean (2.55×10^{15} mol; SARMIENTO and GRUBER, 2006) and the phosphate removal flux (120.6×10^{10} mol yr⁻¹⁰; Tab. 5). In contrast to this estimate, the residence time results as 6 kyr applying the phosphorus removal flux (45.5×10^{10} mol yr⁻¹, section 2.3). In the later case, phosphorus bound in bioturbated surface sediments is regarded as part of the oceanic phosphorus inventory. Considering that up to 30.7×10^{10} mol yr⁻¹ of the total burial flux may be induced by the deposition of terrigenous particles, the remaining marine removal flux ($\geq 15 \times 10^{10}$ mol yr⁻¹) would indicate a residence time of ≤ 17 kyr.

The flux imbalance ($\geq 11.6 \times 10^{10} \text{ mol yr}^{-1}$) suggests that the ocean is currently losing dissolved phosphate at a rate of $\geq 4.5 \text{ \% kyr}^{-1}$. Assuming a linear decrease over the Holocene, the phosphate inventory of the ocean would have been $\geq 4.6 \times 10^{15} \text{ mol}$ at the last deglaciation (18 kyr b. p.), viz. $\geq 82 \text{ \%}$ higher than the present inventory. The shelf-nutrient hypothesis (BROECKER, 1982) suggests that the loss of the continental margin sink during glacial sea-level low-stands should result in a transfer of dissolved phosphate into the deep ocean and an increase in the dissolved phosphate inventory of the glacial ocean. Moreover, continental weathering rates may have been drastically enhanced at the last deglaciation by the exposure of finely ground material (VANCE et al., 2009). The enhanced release of phosphate via continental weathering and the reduced burial of phosphorus at continental margins may have drastically increased the dissolved phosphate inventory of the ocean during the last glacial and the deglaciation. A number of recent studies suggest that the glacial phosphate inventory might have been much higher than today (FILIPPELLI et al., 2007; TAMBURINI and FÖLLMI, 2009; WALLMANN, 2003). The imbalance in the modern phosphorus mass balance derived above is adding further evidence supporting this hypothesis.

4 Conclusions

Phosphate is preferentially retained in pelagic deep-sea sediments where extended oxygen exposure times favor the degradation of particulate organic matter and the uptake of phosphate in manganese and iron oxides and hydroxides. Enhanced C : P regeneration ratios observed in the deep water column (ANDERSON and SARMIENTO, 1994) probably reflect the preferential burial of phosphorus in pelagic sediments.

Excess phosphate is released from continental margin sediments deposited in low-oxygen environments. The oxygen threshold value for the enhanced release of dissolved phosphate is $\sim 20 \mu\text{M}$ (Fig. 2). Benthic phosphate fluxes strongly increase when dissolved oxygen concentrations fall below this value in ambient bottom waters.

The marine phosphorus budget of the pre-human modern ocean is unbalanced since the accumulation of phosphorus in marine sediments and altered oceanic crust exceeds the continental input of particulate and dissolved phosphorus. This imbalance suggests a decline in the dissolved phosphate inventory of the global ocean over the Holocene. The glacial dissolved phosphate level was probably higher than today because the phosphorus accumulation at the continental shelves was reduced by the low sea-level stand (BROECKER, 1982). Peak phosphate concentrations may have been reached during the last deglaciation when phosphate was released into the ocean by the weathering of finely ground material left behind by the demise of the continental ice shields (VANCE et al., 2009). Sediment records from the Southern Ocean and the equatorial Pacific Ocean indicate a maximum in marine export production at the last deglaciation (FILIPPELLI et al., 2007) that may be related to the deglacial weathering pulse enhancing the phosphate inventory of the global ocean. The current decline in dissolved phosphate may reflect the decay of the deglacial phosphate pulse.

Human activities have increased the riverine flux of dissolved phosphate into the ocean (HARRISON et al., 2005) while the flux of particulate phosphorus has been reduced by river dams (SEITZINGER et al., 2005). The net anthropogenic effect on riverine phosphorus fluxes is uncertain. Moreover, the oxygen level in the ocean is currently

declining in response to anthropogenic CO₂ emissions and global warming. The expansion of oxygen minimum zones (STRAMMA et al., 2008) may increase the benthic fluxes of phosphate at the continental margins. The further expansion of oxygen minimum zones predicted by ocean modeling (OSCHLIES et al., 2008) may be amplified by the enhanced benthic phosphate release from margin sediments in a positive feed-back loop. Since most of the marine phosphate originates from continental margin sediments, the oxygen-driven increase in benthic margin fluxes may have a significant effect on the future marine phosphate inventory.

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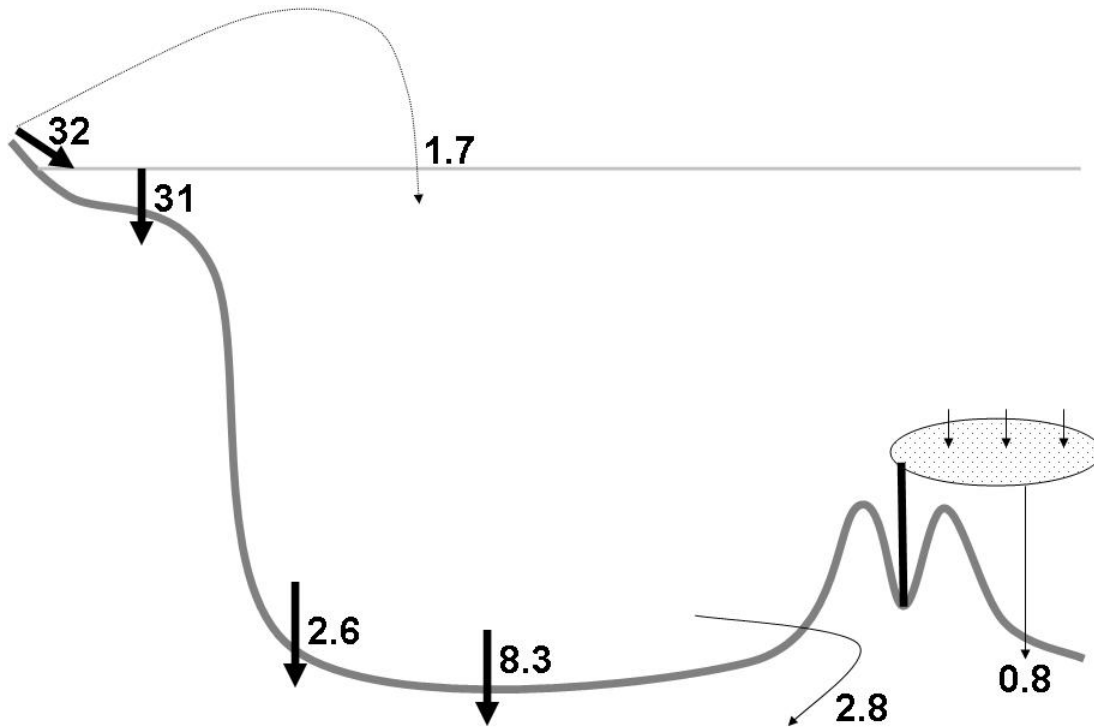


Fig 1. Total phosphorus budget of the modern ocean. Pre-anthropogenic fluxes are given in $10^{10} \text{ mol P yr}^{-1}$. The fluxes from left to right are: input of particulate riverine P, riverine dissolved P and ice-rafted particulate P (32); accumulation of P in shelf and slope sediments (31); accumulation of P in hemipelagic sediments (2.6); deposition of eolian P at the sea surface (1.7); accumulation of P in pelagic sediments (8.3); fixation of P in altered ocean crust via ridge flank circulation (2.8); deposition of P adsorbed to hydrothermal plume particles (0.8).

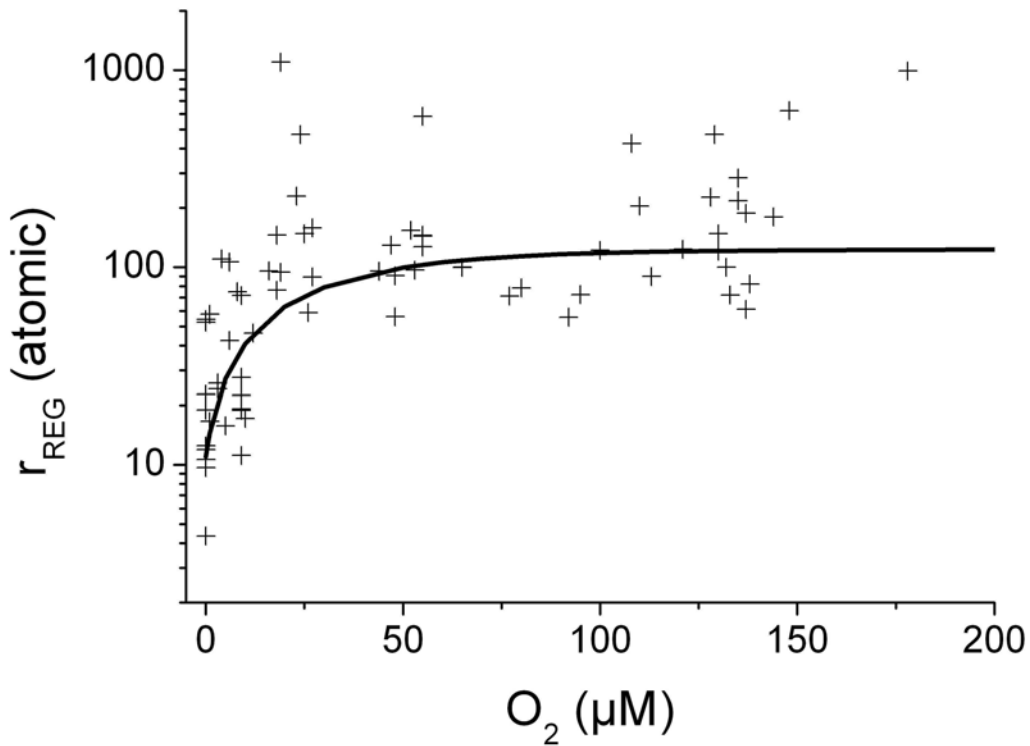


Fig. 2: C : P regeneration ratio (r_{REG}) in continental margin sediments as function of the dissolved oxygen concentration in ambient bottom waters. r_{REG} is calculated dividing the depth-integrated rate of organic matter degradation by the benthic flux of dissolved phosphate into the bottom water. Data were taken from HARTNETT and DEVOL (2003), DEVOL and CHRISTENSEN (1993), BERELSON et al. (1996), MCMANUS et al. (1997), INGALL and JAHNKE (1994), and INGALL and JAHNKE (1997). The solid line was fitted through the data using the exponential equation presented in the text.

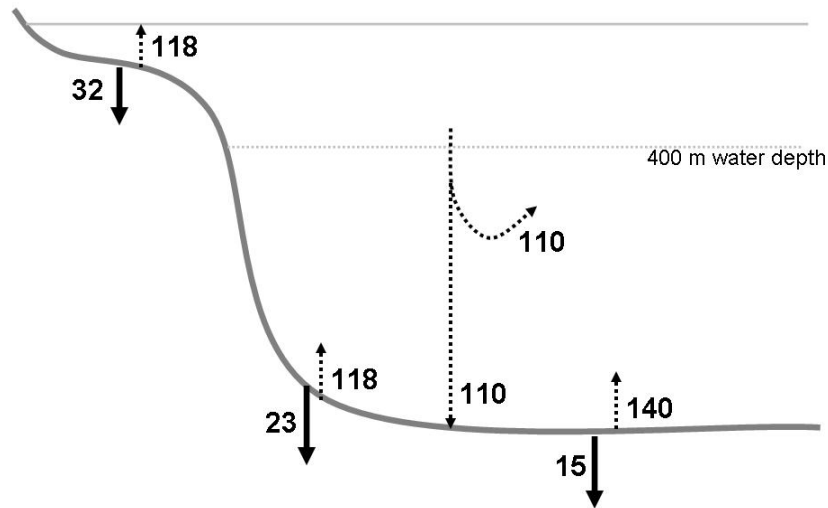


Fig. 3. Atomic ratios of particulate organic carbon to total P in the global ocean. Solid arrows indicate POC : P burial flux ratios in marine sediments deposited at the continental shelf and slope (32), continental rise (23), and deep-sea floor (15). Dotted arrows indicate the POC : P regeneration ratios in marine surface sediments (margin: 118, deep-sea floor 140) and in the deep water column (>400 m water depth: 110) and the POP : P ratio in marine particles sinking to the deep-sea floor (110).

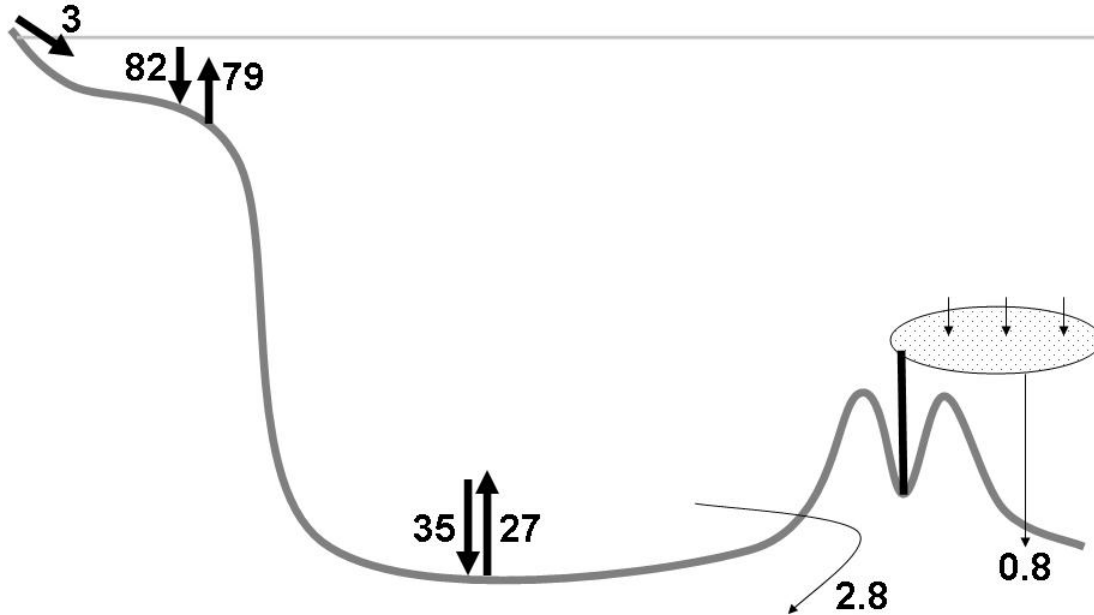


Fig 4. Dissolved phosphorus budget of the modern ocean. Pre-anthropogenic fluxes are given in 10^{10} mol P yr^{-1} . The fluxes from left to right are: input of riverine dissolved P (3); rain rate of marine POP to the margin seafloor (82); benthic phosphate flux from margin sediments (79); rain rate of marine POP to the deep-sea seafloor (35; for >1000 m water depth); benthic phosphate flux from deep-sea sediments (27); fixation of P in altered ocean crust via ridge flank circulation (2.8); deposition of P adsorbed to hydrothermal plume particles (0.8).

