

## Phosphorus imbalance in the global ocean?

Klaus Wallmann<sup>1</sup>

Received 6 August 2009; revised 10 June 2010; accepted 10 September 2010; published 21 December 2010.

[1] The phosphorus budget of the prehuman 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 prehuman global ocean. The ocean is losing dissolved phosphate at a rate of  $\geq 11.6 \times 10^{10}$  mol yr<sup>-1</sup> corresponding to a decline in the phosphate inventory of  $\geq 4.5\%$  kyr<sup>-1</sup>. 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 uptake 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  $\sim 20$   $\mu$ M. Benthic phosphate fluxes increase drastically when oxygen concentrations fall below this value.

**Citation:** Wallmann, K. (2010), Phosphorus imbalance in the global ocean?, *Global Biogeochem. Cycles*, 24, GB4030, doi:10.1029/2009GB003643.

### 1. Introduction

[2] Phosphorus is the limiting nutrient in the oceans on geological timescales. 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 prehuman 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].

[3] 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 a new sequential extraction procedure allowing for a separation of reactive and refractory sedimentary P phases [Ruttenberg, 1992]. The burial of reactive, potentially bioavailable P occurs mainly at the continental margins. The global burial rate of reactive P was estimated as  $8.0\text{--}18.5 \times 10^{10}$  mol yr<sup>-1</sup> applying updated 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

<sup>1</sup>IFM-GEOMAR, Kiel, Germany.

**Table 1.** Modern Preanthropogenic Fluxes of Phosphorus Into the Ocean

	Mass Flux ( $10^{15}$ g yr $^{-1}$ )	Mean P Concentration ( $\mu\text{mol g}^{-1}$ )	P Flux ( $10^{10}$ 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

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 [Benitez-Nelson, 2000; Paytan and McLaughlin, 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.

[4] The present contribution is constraining the preanthropogenic 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, 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 prehuman global ocean (section 4).

## 2. The Phosphorus Budget of the Prehuman Modern Ocean

[5] 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

[6] The natural riverine input of dissolved and particulate phosphorus into the ocean is poorly constrained because of the limited database 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  $1.2 \times 10^{10}$  mol yr $^{-1}$  using the Global Nutrient Export from Watersheds (NEWS) model [Harrison et al., 2005]. The natural flux of dissolved organic phosphorus (DOP) amounts to  $1.8 \times 10^{10}$  mol yr $^{-1}$  [Seitzinger et al., 2005] contributing more than 50% to the total dissolved P input ( $3.0 \times 10^{10}$  mol yr $^{-1}$ ). Most of the riverine P input to the ocean is, however, associated with suspended particles. Beusen et al. [2005] estimate that  $19 \times 10^{15}$  g yr $^{-1}$  of suspended particulate matter reached the oceans before the damming of river systems resulting in a particulate phosphorus flux of  $32 \times 10^{10}$  mol yr $^{-1}$ . The mean P content of river particles calculated from these numbers is  $17 \mu\text{mol P g}^{-1}$ . The P concentration in riverine particles is thus close to the mean P level in continental crustal rocks previously estimated as  $18 \mu\text{mol g}^{-1}$  [Faure, 1998]. It should, however, be noted that continental erosion has been greatly accelerated by agriculture. Considering the effects of human land use, the preanthropogenic flux of riverine particles into the oceans has been estimated as only  $14 \times 10^{15}$  g yr $^{-1}$  [Syvitski et al., 2005]. The preanthropogenic flux of riverine particulate P, thus, results as  $24 \times 10^{10}$  mol yr $^{-1}$  applying the mean particle concentration of  $17 \mu\text{mol P g}^{-1}$  and the preanthropogenic particle flux given by Syvitski et al. [2005].

[7] Additional particulate P is transported to the oceans by eolian dust and ice-rafted material. The preanthropogenic depositional flux of eolian phosphorus has recently been estimated as  $1.7 \times 10^{10}$  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  $\sim 0.74 \times 10^{15}$  g yr $^{-1}$  [Mahowald et al., 2008]. The mass flux of ice-rafted particles has been determined as  $2.9 \times 10^{15}$  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  $5 \times 10^{10}$  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].

[8] 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 preanthropogenic phosphorus budget (Table 1).

### 2.2. Phosphorus Deposition at the Seafloor

[9] The global distribution of total particulate phosphorus in marine surface sediments was presented by Baturin [1988], Baturin and Savenko [1997], and Baturin [2007].

**Table 2.** Burial Flux of Phosphorus at the Modern Seafloor [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

Each of the mean values listed in Table 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.

[10] 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, 2003]. Phosphate adsorption on plume particles removes  $0.8 \times 10^{10}$  mol yr $^{-1}$  [Wheat et al., 1996] while an additional removal flux of  $2.8 \times 10^{10}$  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 ( $3.6 \times 10^{10}$  mol yr $^{-1}$ ) is thus higher than the riverine flux of dissolved phosphorus into the ocean ( $3.0 \times 10^{10}$  mol yr $^{-1}$ ).

### 2.3. Mass Balance of Phosphorus in the Modern Ocean

[11] The available data indicate that the total removal of phosphorus ( $45.5 \times 10^{10}$  mol yr $^{-1}$ ) via hydrothermal activity ( $3.6 \times 10^{10}$  mol yr $^{-1}$ ) and burial at the seafloor ( $41.9 \times 10^{10}$  mol yr $^{-1}$ ; Table 2) is higher than the modern pre-anthropogenic phosphorus input to the global ocean ( $33.7 \times 10^{10}$  mol yr $^{-1}$ ; Table 1). The modern flux imbalance results as  $11.8 \times 10^{10}$  mol yr $^{-1}$  or 35% of the input flux (Figure 1). The mass fluxes of particles (particle input from the continents:  $17.64 \times 10^{15}$  g yr $^{-1}$ , sedimentation:  $18.843 \times 10^{15}$  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  $\text{CaCO}_3$  burial flux at the continental shelf ( $1.0 \times 10^{15}$  g yr $^{-1}$  [Kleyvas, 1997]), the accumulation of pelagic carbonates at the deep seafloor ( $1.0 \times 10^{15}$  g yr $^{-1}$  [Archer, 1996]), and the burial of biogenic opal at the seafloor ( $0.27 \times 10^{15}$  g yr $^{-1}$  [Sarmiento and Gruber, 2006]) contribute significantly to the total sedimentation. Considering the accumulation of these biogenic components ( $2.27 \times 10^{15}$  g yr $^{-1}$ ) and the continental particle export ( $17.64 \times 10^{15}$  g yr $^{-1}$ ; Table 1), the total sedimentation rate at the seafloor should be  $19.91 \times 10^{15}$  g yr $^{-1}$ . The number given in Table 2 is smaller ( $18.843 \times 10^{15}$  g yr $^{-1}$ ) and

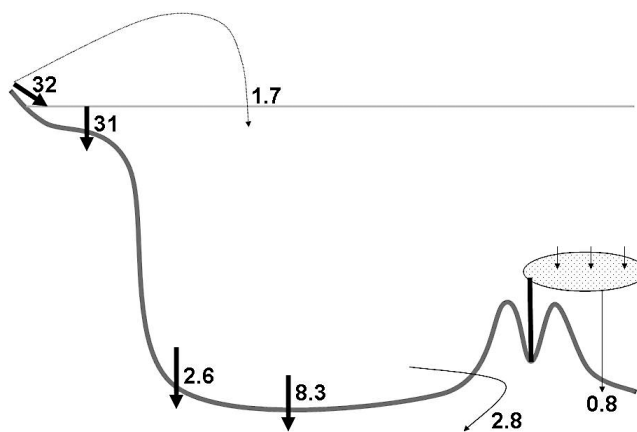
hence the excess P burial indicated by the phosphorus mass balance is not caused by an overestimation of the total sedimentation rate at the seafloor.

[12] 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 (Figure 1). These fluxes are not well constrained such that the apparent imbalance in the phosphorus budget might not be significant. In section 3, 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

[13] 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



**Figure 1.** Total phosphorus budget of the modern ocean. Preanthropogenic fluxes are given in  $10^{10}$  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).

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.

[14] 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.

[15] 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].

[16] Global mean phosphorus concentrations listed in Tables 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

[17] 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  $200\text{--}400 \times 10^{10} \text{ mol yr}^{-1}$  [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].

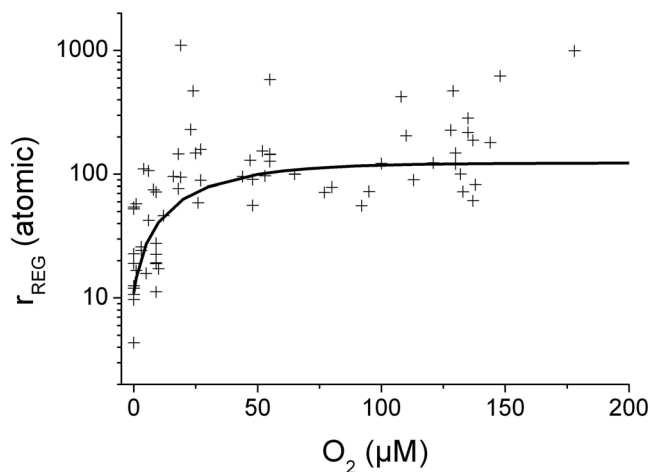
[18] A large fraction of the particulate phosphorus being deposited at the margin seafloor is degraded in surface sediments and transformed into dissolved phosphate. The dissolved phosphate accumulating in sediment pore waters is partly recycled into the overlying bottom water via molecular diffusion and bioirrigation. 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, 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. Figure 2 shows that the ratio between the depth-integrated rate of POC degradation and the benthic phosphate release ( $r_{\text{REG}}$ ) is clearly a function of bottom water oxygenation in continental margin sediments.

[19] Massive amounts of excess phosphate are released under low-oxygen conditions (<20  $\mu\text{M}$ ) whereas the C: P regeneration ratios ( $r_{\text{REG}}$ ) 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, 1997; Slomp *et al.*, 2002, 2004; Slomp and Van Cappellen, 2007; Van Cappellen and Ingall, 1994, 1996; Wallmann, 2003].

[20] The following function was applied to describe the oxygen dependence of the regeneration ratio ( $r_{\text{REG}}$ ):

$$r_{\text{REG}} = \frac{\text{RPOC}}{\text{BenPO}_4} = Y_F + A \cdot \exp\left(-\frac{\text{O}_2}{r}\right) \quad (1)$$

where RPOC is the depth-integrated rate of organic matter degradation in surface sediments and BenPO<sub>4</sub> is the benthic flux of dissolved phosphate into the bottom water. The model parameters were determined as  $Y_F = 123 \pm 24$ ,  $A = -112 \pm 24$ , and  $r = 32 \pm 19$  applying a statistical weighting method (weights =  $1/r_{\text{REG}}$ ). The fit (solid line in Figure 2) indicates that the regeneration ratio under oxic conditions ( $Y_F$ ) is probably higher than the Redfield value.



**Figure 2.** C:P regeneration ratio ( $r_{\text{REG}}$ ) in continental margin sediments as a function of the dissolved oxygen concentration in ambient bottom waters. Here  $r_{\text{REG}}$  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], and *Ingall and Jahnke* [1994, 1997]. The solid line was fitted through the data using the exponential equation presented in the text.

[21] Equation (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  $\text{CO}_2$  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].

[22] 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 (see Table 3). A previous estimate based on sedimentary data yields a value of  $12 \text{ Tmol yr}^{-1}$  for the POC accumulation at continental margins [*Hedges and Keil*, 1995]. The POC burial flux is, however, poorly constrained. A large range of values ( $10\text{--}200 \text{ Tmol yr}^{-1}$ ) 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  $\sim 30\%$  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.

[23] The rain rate of POC to the seafloor (RRPOC) can be estimated considering the burial efficiency of POC. The burial efficiency (BE in percent) is defined as

$$\text{BE} = \frac{\text{APOC}}{\text{RRPOC}} \cdot 100. \quad (3)$$

[24] It is known to depend on sedimentation rate,  $\text{O}_2$  concentrations in ambient bottom waters, and the grain size of sediments [*Burdige*, 2007; *Canfield*, 1993]. BE is very low in sandy shelf sediments ( $\sim 1\%$  [*Burdige*, 2007]) and high in muddy shelf deposits ( $\sim 30\%$  [*Burdige*, 2007; *Canfield*, 1993]). Applying a mean BE value of  $\sim 10\%$ , the rain rate for shelf and slope sediments results as  $\text{RRPOC} = 98 \text{ Tmol yr}^{-1}$ . Applying the same BE value to the hemipelagic sediments deposited at the continental rise, the corresponding value results as  $\text{RRPOC} = 5.8 \text{ Tmol yr}^{-1}$ . The total rain rate at the continental margins is thus  $103.8 \text{ Tmol yr}^{-1}$ . 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 preanthropogenic mass flux of phosphorus bound in riverine, ice-rafted, and eolian particles ( $30.7 \times 10^{10} \text{ mol yr}^{-1}$ ; Table 1), the preanthropogenic terrestrial POC flux to the ocean results as  $17.2 \text{ Tmol yr}^{-1}$ . The rain rate of marine POC to the margin seafloor is calculated by difference as  $86.6 \text{ Tmol yr}^{-1}$ .

[25] This flux is significantly smaller than the POC rain rate to the margin seafloor (0–2000 m water depth) derived by ocean biogeochemical modeling ( $165 \pm 64 \text{ Tmol yr}^{-1}$  [*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 resuspended by strong bottom currents and degraded in the water column. The difference between the benthic bottom-up estimate and

**Table 3.** Particulate Organic Carbon Turnover and Benthic Phosphate Fluxes in Marine Surface Sediments<sup>a</sup>

Sediment Type	Area (10 <sup>6</sup> km <sup>2</sup> )	POC (wt %)	POC/P (Atomic)	APOC (Tmol yr <sup>-1</sup> )	RPOC (Tmol yr <sup>-1</sup> )	r <sub>REG</sub>	BenPO4 (10 <sup>10</sup> mol yr <sup>-1</sup> )
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

<sup>a</sup>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<sub>REG</sub>), 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<sup>-1</sup> [Seiter *et al.*, 2005]) and the corresponding depositional areas for each sediment type.

the top-down estimate derived from ocean modeling may, thus, be related to sediment resuspension.

[26] 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<sup>-1</sup> (Tables 3 and 4). Previous estimates for RPOC in continental margin sediments range in between 40 and 230 Tmol yr<sup>-1</sup> [Burdige, 2007]. The new RPOC value presented in this paper is thus consistent with previous estimates derived from benthic observations.

[27] The ratio between organic carbon mineralization in continental margin sediments and the benthic release of dissolved phosphate (r<sub>REG</sub>) is further constrained applying the following mass balance equation:

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

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<sup>10</sup> mol yr<sup>-1</sup> from the marine POC rain rate (86.6 Tmol yr<sup>-1</sup>) and the Redfield ratio (106: 1). Considering the terrestrial particulate P flux (30.7 × 10<sup>10</sup> mol yr<sup>-1</sup>; Table 1), the total rain of particulate P to the margin seafloor results as 112.4 × 10<sup>10</sup> mol yr<sup>-1</sup>. 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 Tables 2 and 3, and the POC rain rate (RRPOC = 103.8 Tmol yr<sup>-1</sup>) into equation (4), yields an atomic r<sub>REG</sub> value of 118. This value is higher than the Redfield ratio and consistent with the oxic flux ratio (Y<sub>F</sub> = 123 ± 24) derived from the independent benthic flux data (Figure 1). The good match between r<sub>REG</sub> and Y<sub>F</sub> confirms that the rain rates and accumulation rates applied in equation (4) are representative for the global continental margins.

[28] Applying the phosphorus mass balance (BenPO<sub>4</sub> = RRP - AP), the total benthic flux of dissolved phosphate (BenPO<sub>4</sub>) from shelf, slope, and rise sediments into the water column is finally calculated as 79 × 10<sup>10</sup> mol yr<sup>-1</sup>. The individual contribution of shelf and slope sediments and hemipelagic sediments is calculated applying the r<sub>REG</sub> value

to the corresponding RPOC rates (see Table 3). The benthic phosphate fluxes are calculated from a mass balance assuming that the entire particulate P delivered from the continents (30.7 × 10<sup>10</sup> mol yr<sup>-1</sup>; Table 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 × 10<sup>10</sup> mol yr<sup>-1</sup> [Sutula *et al.*, 2004]) and the desorption of phosphate from eolian particles (~0.2 × 10<sup>10</sup> mol yr<sup>-1</sup> [Mahowald *et al.*, 2008]).

[29] Overall, the phosphorus turnover at continental margins is remarkably well balanced. The total burial of phosphorus (33.6 × 10<sup>10</sup> mol yr<sup>-1</sup>) is as high as the continental input of dissolved and particulate P (33.7 × 10<sup>10</sup> mol yr<sup>-1</sup>). 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.

[30] 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 sea-

**Table 4.** Global Fluxes of Particulate Organic Carbon (in Tmol yr<sup>-1</sup>) at Continental Margins and in Open Oceans Considered in the Phosphorus Mass Balance<sup>a</sup>

	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

<sup>a</sup>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 equation (2).

floor and the POC burial flux (Table 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 ( $r_{\text{REG}} = 123$ ; Figure 1), and the terrestrial input of particulate P to the ocean ( $30.7 \times 10^{10} \text{ mol yr}^{-1}$ ; Table 1). While, the benthic phosphate flux is close to the estimate derived above, the burial flux of P is enhanced by a factor of  $\sim 3$ . With this estimate, the margins would serve as a net phosphorus sink and the burial flux at the margins would be  $\sim 3$  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

[31] The export production of POC into the deep ocean, the rain rate of POC to the deep seafloor ( $>2000 \text{ m}$  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 seafloor ( $>1000 \text{ m}$  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]; Table 3). Top-down model results and bottom-up benthic data are, thus, broadly consistent for the open ocean and the deep seafloor (Table 4).

[32] 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  $\text{O}_2$  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.

[33] A simple mass balance is set up to control this hypothesis. The C/P regeneration ratio observed in the water column data ( $r_{\text{REG}} = 117$ ) is related to the POC export

production at 400 m water depth (EXPOC400) and the POC burial rate ( $\text{APOC} = 1.83 \text{ Tmol yr}^{-1}$ ) as

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

where  $r_{\text{EX}}$  is the C: P ratio of organic matter exported to  $>400 \text{ m}$  water depth ( $\sim 106$ ) and  $r_{\text{B}}$  the POC/P burial ratio. EXPOC400 is estimated as  $90\text{--}300 \text{ Tmol yr}^{-1}$  from the export production at 100 m water depth ( $\text{EXPOC} = 546 \pm 212 \text{ Tmol yr}^{-1}$ ) applying the Martin equation ( $\text{EXPOC400}/\text{EXPOC} = (400/100)^{-b}$ ) [Martin *et al.*, 1987] with  $b = 0.82 \pm 0.16$  [Berelson, 2001].

[34] Solving for  $r_{\text{B}}$ :

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

and inserting the values given above, results in  $r_{\text{B}} = 6\text{--}20$ .

[35] Sedimentary data [Baturin, 2007] indeed show that the POC/P burial ratio ( $r_{\text{B}}$ ) is significantly reduced in pelagic sediments (Table 3). The POC/P burial ratio in pelagic sediments ( $r_{\text{B}} = 5\text{--}18$ ) complies with the range of values predicted by the mass balance ( $r_{\text{B}} = 6\text{--}20$ ). 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.

[36] In equation (6), Redfield stoichiometry is assumed for the particles sinking into the deep ocean ( $r_{\text{EX}} = 106$ ). 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  $>300 \text{ m}$  water depth ( $r_{\text{EX}} \approx 175$ ) 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 ( $>300 \text{ m}$ ), 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 midwater traps at the European continental margin (580 and 600 m water depth).

[37] 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  $r_{\text{B}} = 16.8$  [Baturin, 2007] while the best estimate for the export production of POC at 400 m water depth is calculated as  $\text{EXPOC400} = 175 \text{ Tmol yr}^{-1}$  applying the Martin relation

with  $b = 0.82$  and  $\text{EXPOC} = 546 \text{ Tmol yr}^{-1}$ . Solving equation (6) for  $r_{\text{EX}}$ :

$$r_{\text{EX}} = \frac{\text{EXPOC}400 \cdot r_{\text{B}} \cdot r_{\text{REG}}}{\text{EXPOC}400 \cdot r_{\text{B}} + \text{APOC} \cdot (r_{\text{REG}} - r_{\text{B}})} \quad (7)$$

and inserting the values given above results in  $r_{\text{EX}} = 110$ . 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.

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

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

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

[39] Benthic fluxes of dissolved phosphate at the deep seafloor were determined by a benthic chamber deployment in the eastern North Pacific [Smith *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 *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  $\sim 170$ . 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  $r_{\text{REG}}$  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  $\sim 200$ . 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 bioirrigation may contribute to the overall flux. The difference between the  $r_{\text{REG}}$  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 seafloor 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 (Figure 3).

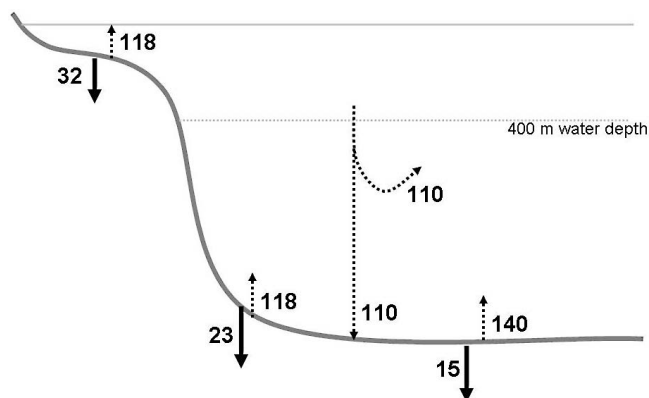
[40] Pelagic surface sediments are exposed to high oxygen concentrations over extended periods of time because of low sedimentation and oxygen consumption rates. The degradation of organic matter is promoted by these extended oxygen exposure times [Hedges *et al.*, 1999; Meile and Van Cappellen, 2005] 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.

[41] 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 seafloor thus serves as phosphorus sink contributing significantly to the imbalance in the oceanic phosphorus cycle.

### 3.4. Dissolved Phosphate Budget of the Global Ocean

[42] The input of dissolved phosphate to the global oceans is clearly dominated by the benthic turnover in marine surface sediments (Figure 4). The total benthic release of dissolved phosphate from marine sediments ( $106 \times 10^{10} \text{ mol yr}^{-1}$ ; Table 3) is much higher than the input of riverine dissolved phosphorus to the ocean ( $3 \times 10^{10} \text{ mol yr}^{-1}$ ; Table 1). The benthic fluxes are dominated by the contribution of shelf and slope sediments (Table 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 ( $109 \times 10^{10} \text{ mol yr}^{-1}$ ; Table 5) is estimated to be smaller than the removal flux via deposition of marine organic matter at the seafloor and via hydrothermal activity ( $120.6 \times 10^{10} \text{ mol yr}^{-1}$ ; Table 5). 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 Table 5 are conservative estimates being approximately two times lower than the corresponding removal fluxes derived from biogeochemical ocean model-





**Figure 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 seafloor (15). Dotted arrows indicate the POC: P regeneration ratios in marine surface sediments (margin, 118; deep seafloor, 140) and in the deep water column (>400 m water depth, 110) and the POP: P ratio in marine particles sinking to the deep seafloor (110).

ing [Dunne *et al.*, 2007]. Moreover, the benthic fluxes are based on conservative estimates of the regeneration ratio. Benthic chamber deployments (section 3.2; Figure 1) and pore water gradients (section 3.3) indicate higher  $r_{\text{REG}}$  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 Table 5. Considering the available evidence, it is very likely that the phosphate and phosphorus budgets are not at steady state in the prehuman global ocean.

[43] 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.

[44] 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 ( $2.55 \times 10^{15}$  mol [Sarmiento and Gruber, 2006]) and the phosphate removal flux ( $120.6 \times 10^{10}$  mol yr<sup>-10</sup>; Table 5). In contrast to this estimate, the residence time results as 6 kyr applying the phosphorus removal flux ( $45.5 \times 10^{10}$  mol yr<sup>-1</sup>; 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  $30.7 \times 10^{10}$  mol yr<sup>-1</sup> 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<sup>-1</sup>) would indicate a residence time of  $\leq 17$  kyr.

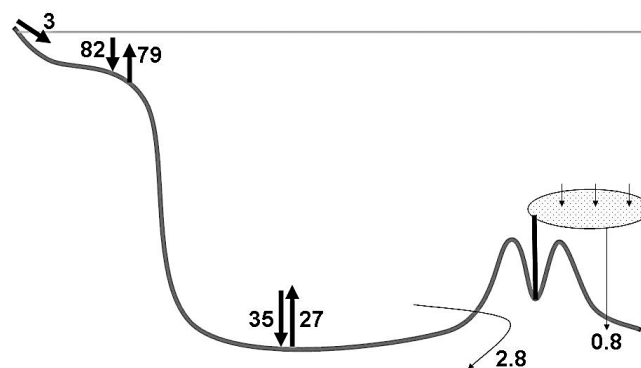
[45] The flux imbalance ( $\geq 11.6 \times 10^{10}$  mol yr<sup>-1</sup>) suggests that the ocean is currently losing dissolved phosphate at a rate of  $\geq 4.5\%$  kyr<sup>-1</sup>. Assuming a linear decrease over the Holocene, the phosphate inventory of the ocean would have been  $\geq 4.6 \times 10^{15}$  mol at the last deglaciation (18 ka), viz.

$\geq 82\%$  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

[46] 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.

[47] 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  $\sim 20$   $\mu\text{M}$  (Figure 2). Benthic phosphate fluxes strongly increase when dissolved oxygen concentrations fall below this value in ambient bottom waters.



**Figure 4.** Dissolved phosphorus budget of the modern ocean. Preanthropogenic fluxes are given in  $10^{10}$  mol P yr<sup>-1</sup>. 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).

**Table 5.** Dissolved Phosphorus Budget of the Prehuman Global Ocean

	Flux ( $10^{10}$ mol $\text{yr}^{-1}$ )
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 seafloor	35
Hydrothermal removal of dissolved phosphate	3.6
Total	120.6

[48] The marine phosphorus budget of the prehuman 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.

[49] 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  $\text{CO}_2$  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 feedback 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.

[50] **Acknowledgments.** This work has been supported by the DFG through the SFB 754 "Climate-Biogeochemistry Interactions in the Tropi-

cal Ocean" at Kiel University. I would like to thank colleges from IFM-GEOMAR (A. Oschlies, C. Hensen, and A. Dale) for inspiring discussions on phosphorus cycling in the global ocean and the anonymous reviewers for their helpful comments.

## References

- Algeo, T. J., and E. D. Ingall (2007), Sedimentary  $\text{C}_{\text{org}}:\text{P}$  ratios, paleocean ventilation, and Phanerozoic atmospheric  $\text{pO}_2$ , *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 256, 130–155, doi:10.1016/j.palaeo.2007.02.029.
- Anderson, L. A., and J. L. Sarmiento (1994), Redfield ratios of remineralization determined by nutrient data analysis, *Global Biogeochem. Cycles*, 8(1), 65–80, doi:10.1029/93GB03318.
- Anderson, L. D., M. L. Delaney, and K. L. Faul (2001), Carbon to phosphorus ratios in sediments: Implications for nutrient cycling, *Global Biogeochem. Cycles*, 15(1), 65–79, doi:10.1029/2000GB001270.
- Antia, A. N. (2005), Solubilization of particles in sediment traps: Revisiting the stoichiometry of mixed layer export, *Biogeochemistry*, 2, 189–204, doi:10.5194/bg-2-189-2005.
- Archer, D. E. (1996), An atlas of the distribution of calcium carbonate in sediments of the deep sea, *Global Biogeochem. Cycles*, 10(1), 159–174, doi:10.1029/95GB03016.
- Baturin, G. N. (1988), Disseminated phosphorus in oceanic sediments—A review, *Mar. Geol.*, 84, 95–104, doi:10.1016/0025-3227(88)90127-2.
- Baturin, G. N. (2007), Issue of the relationship between primary productivity of organic carbon in ocean and phosphate accumulation (Holocene–Late Jurassic), *Lithol. Miner. Resour.*, 42(4), 318–348, doi:10.1134/S0024490207040025.
- Baturin, G. N., and V. S. Savenko (1997), Phosphorus in oceanic sedimentogenesis, *Oceanology, Engl. Transl.*, 37(1), 107–113.
- Benitez-Nelson, C. R. (2000), The biogeochemical cycling of phosphorus in marine systems, *Earth Sci. Rev.*, 51, 109–135, doi:10.1016/S0012-8252(00)00018-0.
- Berelson, W. M. (2001), The flux of particulate organic carbon into the ocean interior: A comparison of four U. S. JGOFS regional studies, *Oceanography*, 14, 59–67.
- Berelson, W. M., J. McManus, K. H. Coale, K. S. Johnson, T. Kilgore, D. Burdige, and C. Pilska (1996), Biogenic matter diagenesis on the sea floor: A comparison between two continental margin transects, *J. Mar. Res.*, 54, 731–762, doi:10.1357/0022240963213673.
- Berner, R. A., and J.-J. Rao (1994), Phosphorus in sediments of the Amazon River and estuary: Implications for the global flux of phosphorus to the sea, *Geochim. Cosmochim. Acta*, 58, 2333–2339, doi:10.1016/0016-7037(94)90014-0.
- Berner, R. A., K. C. Ruttenger, E. D. Ingall, and J.-L. Rao (1993), The nature of phosphorus burial in modern marine sediments, in *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*, vol. 14, edited by R. Wollast, F. T. Mackenzie, and L. Chou, pp. 365–378, Springer, Berlin.
- Beusen, A. H. W., A. L. M. Dekkers, A. F. Bouwman, W. Ludwig, and J. Harrison (2005), Estimation of global river transport to sediments and associated particulate C, N, and P, *Global Biogeochem. Cycles*, 19, GB4S05, doi:10.1029/2005GB002453.
- Broecker, W. S. (1982), Glacial to interglacial changes in ocean chemistry, *Prog. Oceanogr.*, 11, 151–197, doi:10.1016/0079-6611(82)90007-6.
- Burdige, D. A. (2007), 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.
- Canfield, D. E. (1993), Organic matter oxidation in marine sediments, in *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*, vol. 14, edited by R. Wollast, F. T. Mackenzie, and L. Chou, pp. 333–363, Springer, Berlin.
- Colman, A. S., and H. D. Holland (2000), The global diagenetic flux of phosphorus from marine sediments to the oceans: Redox sensitivity and the control of atmospheric oxygen levels, in *Marine Authigenesis: From Global to Microbial, Spec. Publ. SEPM Soc. Sediment. Geol.*, 66, 53–75.
- Delaney, M. L. (1998), Phosphorus accumulation in marine sediments and the oceanic phosphorus cycle, *Global Biogeochem. Cycles*, 12(4), 563–572, doi:10.1029/98GB02263.
- Devol, A. H., and J. P. Christensen (1993), Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific, *J. Mar. Res.*, 51, 345–372, doi:10.1357/0022240933223765.
- Dunne, J. P., J. L. Sarmiento, and A. Gnanadesikan (2007), A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor, *Global Biogeochem. Cycles*, 21, GB4006, doi:10.1029/2006GB002907.

- Faul, K. L., A. Paytan, and M. L. Delaney (2005), Phosphorus distribution in sinking oceanic particulate matter, *Mar. Chem.*, *97*, 307–333, doi:10.1016/j.marchem.2005.04.002.
- Faure, G. (1998), *Principles and Applications of Geochemistry*, Simon and Schuster, New York.
- Filippelli, G. M. (1997), Controls on phosphorus concentration and accumulation in oceanic sediments, *Mar. Geol.*, *139*, 231–240, doi:10.1016/S0025-3227(96)00113-2.
- Filippelli, G. M., and M. L. Delaney (1994), The oceanic phosphorus cycle and continental weathering during the Neogene, *Paleoceanography*, *9*(5), 643–652, doi:10.1029/94PA01453.
- Filippelli, G. M., J. C. Latimer, R. W. Murray, and J.-A. Flores (2007), Productivity records from the Southern Ocean and the equatorial Pacific Ocean: Testing the glacial shelf-nutrient hypothesis, *Deep Sea Res., Part II*, *54*, 2443–2452, doi:10.1016/j.dsr2.2007.07.021.
- Föllmi, K. B. (1996), The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits, *Earth Sci. Rev.*, *40*, 55–124, doi:10.1016/0012-8252(95)00049-6.
- Föllmi, K. B., H. Weissert, and A. Lini (1993), Nonlinearities in phosphogenesis and phosphorus-carbon coupling and their implications for global change, in *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*, vol. 14, edited by R. Wollast, F. T. Mackenzie, and L. Chou, pp. 447–474, Springer, Berlin.
- Froelich, P. N., M. L. Bender, N. A. Luedtke, G. R. Heath, and T. DeVries (1982), The marine phosphorus cycle, *Am. J. Sci.*, *282*, 474–511, doi:10.2475/ajs.282.4.474.
- Giraud, X., C. Le Quéré, and L. C. da Cunha (2008), Importance of the coastal nutrient supply for global ocean biogeochemistry, *Global Biogeochem. Cycles*, *22*, GB2025, doi:10.1029/2006GB002717.
- Harrison, J. A., S. P. Seitzinger, A. F. Bouwman, N. F. Caraco, A. H. W. Beusen, and C. J. Vörösmarty (2005), Dissolved inorganic phosphorus export to the coastal zone: Results from a spatially explicit, global model, *Global Biogeochem. Cycles*, *19*, GB4S03, doi:10.1029/2004GB002357.
- Hartnett, H. E., and A. H. Devol (2003), Role of a strong oxygen-deficient zone in the preservation and degradation of organic matter: A carbon budget for the continental margin of northwest Mexico and Washington State, *Geochim. Cosmochim. Acta*, *67*, 247–264, doi:10.1016/S0016-7037(02)01076-1.
- Hedges, J. I., and R. G. Keil (1995), Sedimentary organic matter preservation: An assessment and speculative synthesis, *Mar. Chem.*, *49*, 81–115, doi:10.1016/0304-4203(95)00008-F.
- Hedges, J. H., F. S. Hu, A. H. Devol, H. E. Hartnett, E. Tsamakidis, and R. G. Keil (1999), Sedimentary organic matter preservation: A test for selective degradation under oxic conditions, *Am. J. Sci.*, *299*, 529–555, doi:10.2475/ajs.299.7-9.529.
- Hensen, C., H. Landenberger, M. Zabel, and H. D. Schulz (1998), Quantification of diffusive benthic fluxes of nitrate, phosphate, and silicate in the southern Atlantic Ocean, *Global Biogeochem. Cycles*, *12*(1), 193–210.
- Ingall, E. D., and R. A. Jahnke (1994), Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted waters, *Geochim. Cosmochim. Acta*, *58*, 2571–2575, doi:10.1016/0016-7037(94)90033-7.
- Ingall, E. D., and R. A. Jahnke (1997), Influence of water-column anoxia on the elemental fractionation of carbon and phosphorus during sediment diagenesis, *Mar. Geol.*, *139*, 219–229, doi:10.1016/S0025-3227(96)00112-0.
- Ingall, E. D., and P. Van Cappellen (1990), Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments, *Geochim. Cosmochim. Acta*, *54*, 373–386, doi:10.1016/0016-7037(90)90326-G.
- Ingall, E. D., R. M. Bustin, and P. Van Cappellen (1993), Influence of water column anoxia on the burial and preservation of carbon and phosphorus in marine shales, *Geochim. Cosmochim. Acta*, *57*, 303–316, doi:10.1016/0016-7037(93)90433-W.
- Kleypas, J. A. (1997), Modeled estimates of global reef habitat and carbonate production since the Last Glacial Maximum, *Paleoceanography*, *12*(4), 533–545, doi:10.1029/97PA01134.
- Mahowald, N., et al. (2008), Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts, *Global Biogeochem. Cycles*, *22*, GB4026, doi:10.1029/2008GB003240.
- Martin, J. H., G. A. Knauer, D. M. Karl, and W. W. Broenkow (1987), VERTEX: Carbon cycling in the northeast Pacific, *Deep Sea Res., Part A*, *34*, 267–285, doi:10.1016/0198-0149(87)90086-0.
- McManus, J., W. M. Berelson, K. H. Coale, K. S. Johnson, and T. E. Kilgore (1997), Phosphorus regeneration in continental margin sediments, *Geochim. Cosmochim. Acta*, *61*, 2891–2907, doi:10.1016/S0016-7037(97)00138-5.
- Meile, C., and P. Van Cappellen (2005), Particle age distributions and O<sub>2</sub> exposure times: Timescales in bioturbated sediments, *Global Biogeochem. Cycles*, *19*, GB3013, doi:10.1029/2004GB002371.
- Najjar, R. G., et al. (2007), Impact of circulation on export production, dissolved organic matter, and dissolved oxygen in the ocean: Results from Phase II of the Ocean Carbon-cycle Model Intercomparison Project (OCMIP-2), *Global Biogeochem. Cycles*, *21*, GB3007, doi:10.1029/2006GB002857.
- Oschlies, A., K. G. Schulz, U. Riebesell, and A. Schmittner (2008), Simulated 21st century's increase in oceanic suboxia by CO<sub>2</sub>-enhanced biotic carbon export, *Global Biogeochem. Cycles*, *22*, GB4008, doi:10.1029/2007GB003147.
- Paytan, A., and K. McLaughlin (2007), The oceanic phosphorus cycle, *Chem. Rev.*, *107*, 563–576, doi:10.1021/cr0503613.
- Raiswell, R., M. Tranter, L. G. Benning, M. Siebert, R. De'ath, P. Huybrechts, and T. Payne (2006), Contributions from glacially derived sediment to the global iron (oxyhydr)oxide cycle: Implications for iron delivery to the oceans, *Geochim. Cosmochim. Acta*, *70*, 2765–2780, doi:10.1016/j.gca.2005.12.027.
- Redfield, A. C. (1958), The biological control of chemical factors in the environment, *Am. Sci.*, *46*, 205–221.
- Ruttenberg, K. C. (1992), Development of a sequential extraction method for different forms of phosphorus in marine sediments, *Limnol. Oceanogr.*, *37*(7), 1460–1482, doi:10.4319/lo.1992.37.7.1460.
- Ruttenberg, K. C. (1993), Reassessment of the oceanic residence time of phosphorus, *Chem. Geol.*, *107*, 405–409, doi:10.1016/0009-2541(93)90220-D.
- Ruttenberg, K. C., and R. A. Berner (1993), Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments, *Geochim. Cosmochim. Acta*, *57*, 991–1007, doi:10.1016/0016-7037(93)90035-U.
- Sarmiento, J. L., and N. Gruber (2006), *Ocean Biogeochemical Cycles*, Princeton Univ. Press, Princeton, N. J.
- Seiter, K., C. Hensen, and M. Zabel (2005), Benthic carbon mineralization on a global scale, *Global Biogeochem. Cycles*, *19*, GB1010, doi:10.1029/2004GB002225.
- Seitzinger, S. P., J. A. Harrison, E. Dumont, A. H. W. Beusen, and A. F. Bouwman (2005), 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*, GB4S01, doi:10.1029/2005GB002606.
- Slomp, C. P., and P. Van Cappellen (2004), Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact, *J. Hydrol.*, *295*, 64–86, doi:10.1016/j.jhydrol.2004.02.018.
- Slomp, C. P., and P. Van Cappellen (2007), The global marine phosphorus cycle: Sensitivity to oceanic circulation, *Biogeosciences*, *4*, 155–171, doi:10.5194/bg-4-155-2007.
- Slomp, C. P., J. Thompson, and G. J. de Lange (2002), Enhanced regeneration of phosphorus during formation of the most recent eastern Mediterranean sapropel (S1), *Geochim. Cosmochim. Acta*, *66*, 1171–1184, doi:10.1016/S0016-7037(01)00848-1.
- Slomp, C. P., J. Thomson, and G. J. de Lange (2004), Controls on phosphorus regeneration and burial during formation of eastern Mediterranean sapropels, *Mar. Geol.*, *203*, 141–159, doi:10.1016/S0025-3227(03)00335-9.
- Smith, K. L., Jr., G. A. White, and M. B. Laver (1979), Oxygen uptake and nutrient exchange of sediments measured in situ using a free vehicle grab respirometer, *Deep Sea Res., Part A*, *26*, 337–346, doi:10.1016/0198-0149(79)90030-X.
- Stramma, L., G. C. Johnson, J. Sprintall, and V. Morholz (2008), Expanding oxygen-minimum zones in the tropical oceans, *Science*, *320*, 655–658, doi:10.1126/science.1153847.
- Sutula, M., T. S. Bianchi, and B. A. McKee (2004), Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico, *Limnol. Oceanogr.*, *49*(6), 2223–2235, doi:10.4319/lo.2004.49.6.2223.
- Syvitski, J. P. M., C. J. Vörösmarty, A. J. Kettner, and P. Green (2005), Impact of humans on the flux of terrestrial sediment to the global coastal ocean, *Science*, *308*, 376–380, doi:10.1126/science.1109454.
- Tamburini, F., and K. B. Föllmi (2009), Phosphorus burial in the ocean over glacial-interglacial time scales, *Biogeosciences*, *6*, 501–513, doi:10.5194/bg-6-501-2009.
- Tsander, I., and C. P. Slomp (2009), 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.
- Tsander, I., C. P. Slomp, and P. Van Cappellen (2008), Glacial-interglacial variations in marine phosphorus cycling: Implications for ocean produc-

- tivity, *Global Biogeochem. Cycles*, 22, GB4004, doi:10.1029/2007GB003054.
- Van Cappellen, P., and E. D. Ingall (1994), Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus, *Paleoceanography*, 9(5), 677–692, doi:10.1029/94PA01455.
- Van Cappellen, P., and E. D. Ingall (1996), Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity, *Science*, 271, 493–496, doi:10.1126/science.271.5248.493.
- Vance, D., D. A. H. Teagle, and G. L. Foster (2009), Variable Quaternary chemical weathering fluxes and imbalance in marine geochemical budgets, *Nature*, 458, 493–496, doi:10.1038/nature07828.
- Wallmann, K. (2003), Feedbacks between oceanic redox states and marine productivity: A model perspective focused on benthic phosphorus cycling, *Global Biogeochem. Cycles*, 17(3), 1084, doi:10.1029/2002GB001968.
- Wheat, C. G., R. A. Feely, and M. J. Mottl (1996), Phosphate removal by oceanic hydrothermal processes: An update of the phosphorus budget in the oceans, *Geochim. Cosmochim. Acta*, 60, 3593–3608, doi:10.1016/0016-7037(96)00189-5.
- Wheat, C. G., J. McManus, M. J. Mottl, and E. Giambalvo (2003), Oceanic phosphorus imbalance: Magnitude of the mid-ocean ridge flank hydrothermal sink, *Geophys. Res. Lett.*, 30(17), 1895, doi:10.1029/2003GL017318.
- Zabel, M., A. Dahmke, and H. D. Schulz (1998), Regional distribution of diffusive phosphate and silicate fluxes through the sediment-water interface: The eastern South Atlantic, *Deep Sea Res., Part I*, 45, 277–300, doi:10.1016/S0967-0637(97)00073-3.

---

K. Wallmann, IFM-GEOMAR, Wischhofst. 1-3, D-24148 Kiel, Germany. (kwallmann@ifm-geomar.de)