

# Phosphorus regeneration vs. burial in sediments of the Arabian Sea

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Received 3 March 2000; received in revised form 13 April 2001; accepted 24 April 2001

## Abstract

Solid-phase phosphorus (P) speciation and benthic phosphate fluxes have been determined in Arabian Sea sediments. Benthic phosphate fluxes are highest in the continental slope sediments, underlying bottom waters with low oxygen concentrations. Organic matter degradation and phosphate desorption from iron oxides do not produce sufficient phosphate to explain these high phosphate fluxes. The potentially high deposition of P associated with fish debris ( $P_{\text{fish}}$ ) in the Arabian Sea, and a good correlation between benthic phosphate fluxes and  $P_{\text{fish}}$  accumulation rates suggest that benthic phosphate fluxes in these sediments are to a large extent governed by dissolution of biogenic apatite. Factors controlling dissolution and preservation of fish debris, therefore, may play an important role in the burial and regeneration of P in continental margin sediments. A sharp decrease of the reactive P accumulation rate with increasing water depth, in combination with rather constant primary productivity rates throughout the northern Arabian Sea, indicates that P burial in continental margin sediments located within the OMZ is more efficient than in deep basin sediments. The effectiveness of P burial is to a large extent regulated by P regeneration occurring in the water column and redeposition processes. Sedimentary phosphorus burial efficiencies, thus, should be interpreted with caution in terms of the environmental conditions. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Arabian Sea; Phosphorus; Phosphorus cycling; Diagenesis; Oxygen minimum zone

## 1. Introduction

Phosphorus is an essential nutrient for the marine ecosystem. On geological time scales the bio-availability of dissolved phosphorus is thought to control biological productivity (Holland, 1978; Howarth et al., 1995; Tyrrell, 1999). Only a small fraction of

particulate phosphorus produced in the euphotic zone is ultimately buried in the sediment, while the remainder is remobilized and reutilized by the marine ecosystem (Broecker and Peng, 1982). Removal of phosphorus from the ocean is solely governed by accumulation in sediments. Accordingly, the processes regulating burial and regeneration of P in marine sediments have received much attention (e.g., Ruttenger and Berner, 1993; Ingall and Jahnke, 1994, 1997; Slomp et al., 1996; McManus et al., 1997; Hensen et al., 1998; Colman and Holland, 2000).

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The flux of particulate P arriving at the sediment water interface consists of a reactive and a non-reactive fraction. It is important to distinguish between these fractions because only the first may potentially be mobilized and become available again for utilization by the biosphere. Non-reactive P, primarily consisting of detrital apatite, usually represents only a small fraction relative to the total accumulating P flux (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996). Reactive P is delivered to the sediment by three major sources (e.g., Froelich et al., 1988; Van Cappellen and Berner, 1988; Van Cappellen and Ingall, 1994), namely (1) organic matter, (2) iron oxides—which have a high sorption capacity for phosphate, and (3) fish debris. Accumulation of phosphorus incorporated into biogenic carbonates is less important compared to these three reactive P sinks (Berner et al., 1993; Delaney, 1998).

Benthic phosphate regeneration in sediments is controlled by P recycling from biogenic debris, Ferredoxin cycling, and authigenic apatite precipitation (e.g., Froelich et al., 1988; Van Cappellen and Berner, 1988). Continental margin sediments are usually characterised by high benthic phosphate fluxes (Krom and Berner, 1981; Froelich et al., 1988; Ingall and Jahnke, 1994; Schuffert et al., 1994; McManus et al., 1997; Colman and Holland, 2000). The reactive P sources responsible for these high phosphate releases, however, have not yet been adequately identified (Froelich et al., 1988; Van Cappellen and Berner, 1988; Schuffert et al., 1994). Ingall and Jahnke (1994) have shown that benthic regeneration of P is more extensive under oxygen depleted bottom waters, resulting in lower P burial efficiencies. Enhanced loss of P from sediments during periods of anoxic bottom water conditions will lead to an increased supply of P into the photic zone, and may stimulate higher rates of new primary productivity (Ingall et al., 1993; Ingall and Jahnke, 1994, 1997).

In this study, P cycling was investigated in Arabian Sea surface sediments. The Arabian Sea is a marine environment characterized by a high monsoon-induced primary productivity and an intensive oxygen minimum zone (OMZ) between 150- and 1250-m water depths (e.g., Wyrki, 1973; Slater and Kroopnick, 1984). These properties make the Arabian Sea a suitable area to study the effects of surface water productivity, water depth, and bottom

water oxygen (BWO) conditions on sedimentary P cycling. The sediments we investigated on the continental slope and the deep basin underlie, respectively, suboxic and well-oxygenated bottom waters. We will focus on two aspects of sedimentary P cycling in the Arabian Sea, namely (1) the origin of high benthic phosphate fluxes in continental slope sediments, and (2) the environmental factors controlling regeneration and retention of solid-phase P.

## 2. Material and methods

### 2.1. Sample locations

During the Netherlands Indian Ocean programme (NIOP) in 1992, boxcores were taken in the northern Arabian Sea. For this study, we selected 16 boxcores, located on the Pakistan continental slope (stations 451, 452, 453, 454, 455), the Murray ridge (stations 463, 464), the Arabian Basin (stations 409, 411, 458, 460 and 466), and Oman Margin (stations 484, 487, 494 and 497). Sample locations and details for the sample sites are given in Fig. 1 and Table 1. BWO concentrations were derived from oxygen measurements at nearby CTD stations. Sedimentation rates were calculated from AMS  $^{14}\text{C}$  dated foraminiferal samples from the base of the boxcores (Passier et al., 1997; Van der Weijden et al., 1999; Table 1), assuming a constant reservoir age of 400 years. The average mass accumulation rates (MAR) for each core were calculated as the product of the sedimentation rate and the average dry bulk density. The error for the MAR is ca. 10–20% (Van der Weijden et al., 1999).

### 2.2. Pore water analysis

Porewater extractions were performed on board within 24 h of core collection according to shipboard routine (De Lange, 1992). The boxcores were vertically sluiced into a glovebox, which was kept under low-oxygen conditions ( $\text{O}_2 < 0.0005$  vol.%) and at a constant near bottom temperature. Under a nitrogen pressure of up to 7 bar, the pore waters were extracted in Reeburgh-type squeezers (Reeburgh, 1967). The shipboard analysis of ammonium, alkalinity and

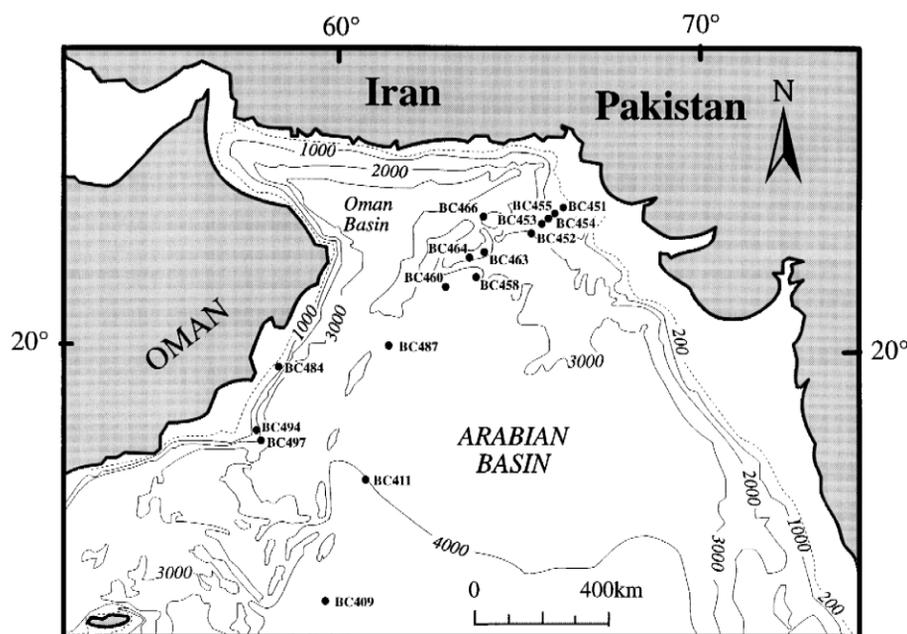


Fig. 1. Sample locations in the northern Arabian Sea of the boxcores used in this study.

phosphate started within 12 h after the extraction of the porewaters. Alkalinity was measured by Gran titration (after Gieskes, 1973). Ammonium and phosphate were analysed on a TRAACS 800 auto-

analyser, after the methods of Strickland and Parsons (1968) and Solarzano (1969), respectively. All determinations were done in duplicate. Relative errors are better than 2%.

Table 1

Location, water depth, bottom water oxygen concentration (BWO), bottom water temperature ( $T_{\text{bottom}}$ ), mass accumulation rate (MAR), and organic carbon ( $C_{\text{org}}$ ) concentration (in top 2 cm) of the box cores used in this study. Boxcores located in the OMZ appear in bold

	Latitude (N)	Longitude (E)	Water depth (m)	BWO ( $\mu\text{M}$ )	$T_{\text{bottom}}$ ( $^{\circ}\text{C}$ )	MAR ( $\text{g cm}^{-2} \text{ ka}^{-1}$ )	$C_{\text{org}}$ top (wt.%)
BC409	13°14'.2	59°30'.6	4338	158.8	1.6		
BC411	16°07'.7	60°45'.2	4016	156.8	1.6		
<b>BC451</b>	<b>23°41'.4</b>	<b>66°02'.9</b>	<b>495</b>	< 2	<b>12.6</b>	<b>12.5</b>	<b>4.1</b>
BC452	22°56'.4	65°28'.1	2001	87.1	3.0	3.8	1.1
BC453	23°14'.0	65°44'.0	1555	39.3	5.0	5.6	1.2
BC454	23°26'.9	65°51'.2	1254	12.5	6.9	6.0	3.4
<b>BC455</b>	<b>23°33'.3</b>	<b>65°57'.2</b>	<b>998</b>	< 2	<b>8.7</b>	<b>6.9</b>	<b>4.3</b>
BC458	21°59'.7	63°48'.8	3000	123.7	1.7	4.0	0.8
BC460	21°43'.2	62°55'.2	3262	125.3	1.7		0.9
<b>BC463</b>	<b>22°33'.6</b>	<b>64°03'.3</b>	<b>970</b>	< 2	<b>8.9</b>	<b>5.2</b>	<b>5.7</b>
BC464	22°15'.0	63°34'.7	1511	34.8	5.3	4.3	1.3
BC466	23°36'.1	63°48'.5	1960	75.4	3.1	5.9	0.9
<b>BC484</b>	<b>19°30'.0</b>	<b>58°25'.8</b>	<b>527</b>	< 2	<b>12.3</b>	<b>3.8</b>	<b>2.3</b>
BC487	19°54'.8	61°43'.3	3566	151.0	1.6	0.8	0.8
BC494	17°42'.0	57°43'.1	2437	88.0	2.2		
BC497	17°26'.7	57°57'.4	1890	82.8	3.4		

Assuming steady state, diffusive (benthic) phosphate fluxes ( $J_p$ ) were estimated with the equation (Berner, 1980):

$$J_p = \phi D_s (dC/dz) \quad (1)$$

where  $\phi$  is the porosity of the upper sediment sample,  $D_s$  the whole sediment diffusion coefficient for phosphate, and  $dC/dz$  the concentration gradient

at the sediment surface, determined as the concentration difference between the uppermost interstitial water sample (1-cm depth) and the bottom water, assuming a linear concentration gradient between these two points. Whole sediment diffusion coefficients ( $D_s$ ) ( $\text{cm}^2 \text{s}^{-1}$ ) can be expressed by

$$D_s = D^* / \theta^2 \quad (2)$$

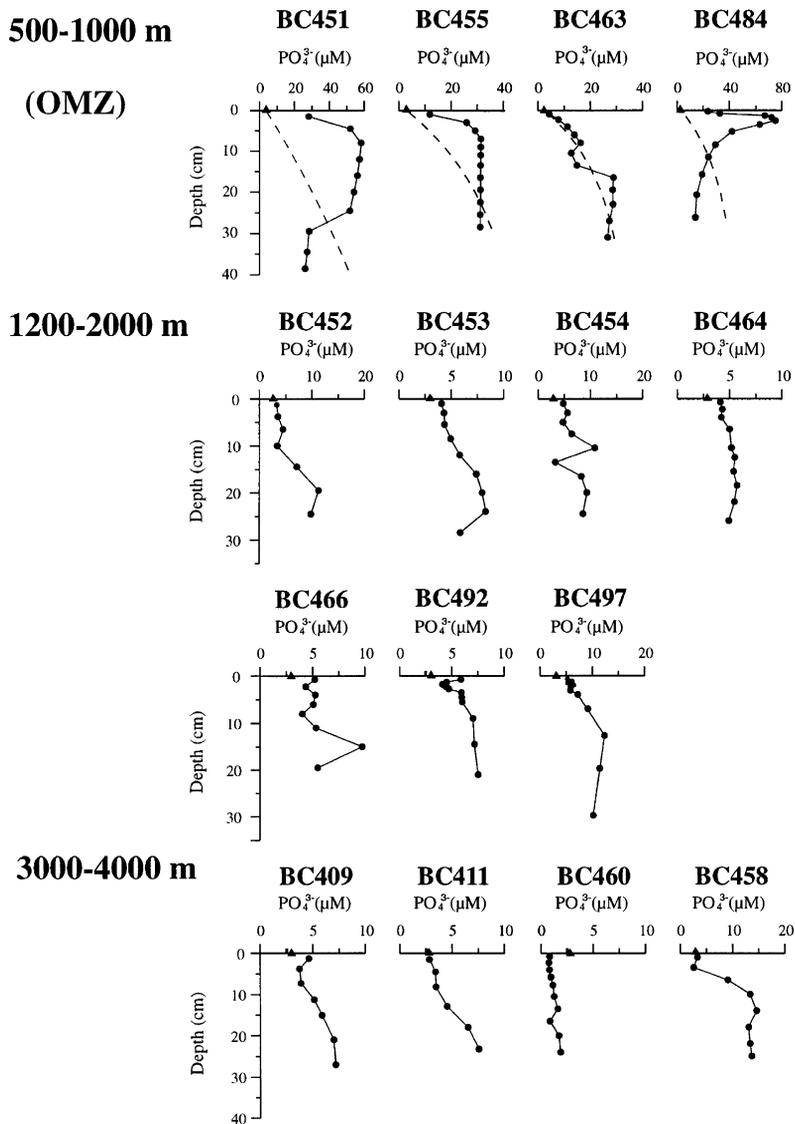


Fig. 2. Porewater profiles of dissolved phosphate ( $\mu\text{M}$ ) for the box cores used in this study (Table 1). Phosphate bottom water concentrations are marked with a  $\blacktriangle$ . The dashed lines indicate the theoretical phosphate profiles resulting from organic matter degradation alone, calculated with Eqs. (4) and (5) (see text).

where  $D^*$  is the diffusion coefficient in seawater and  $\theta$  the tortuosity. Diffusion coefficients ( $7.34 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{HPO}_4^{2-}$  at  $25^\circ\text{C}$ ) were corrected for the in situ bottom water temperatures (Li and Gregory, 1974). The tortuosity of the sediment was estimated with the equation (Boudreau, 1997):

$$\theta^2 = 1 - \ln(\phi^2). \quad (3)$$

Benthic flux calculations based on pore water gradients are subject to several inaccuracies (e.g., Jahnke et al., 1982; Hensen et al., 1998; Colman and Holland, 2000). First, these calculations do not take into account phosphate regenerated at the sediment water interface, which directly diffuses back to the overlying bottom water. Secondly, phosphate transport induced by macrobenthic irrigation is neglected. This may particularly cause an underestimation of the benthic fluxes in relative shallow continental margin sediments, where bioturbation is important (Glud et al., 1994). For this reason, previous studies have confined benthic flux calculations to sample locations deeper than 1000 m (Zabel et al., 1998; Hensen et al., 1998). In this study we included sample sites from 500 m water depth, because the low BWO concentrations inhibit vigorous bioturba-

tion in these sediments (Jannink et al., 1998; Van der Weijden et al., 1999). Thirdly, porewater artifacts may have been introduced during recovery of the carbonate-rich sediments, which may have decreased the phosphate concentrations (Jahnke et al., 1982). This especially affects marine sediments with low interstitial phosphate concentrations (Zabel et al., 1998; Hensen et al., 1998). Finally, the porewater fluxes are potentially subject to seasonal variability (e.g., Krom and Berner, 1981; Hensen et al., 1998), and thus may not represent a steady-state situation. The sediments were sampled between September and November, which is after the monsoon-induced period of high productivity. The estimated benthic fluxes may thus have been higher than the annual average. It should be noted that all but the last of the above mentioned inaccuracies cause an underestimation of the benthic phosphate fluxes.

We recognize that the porewater phosphate data presented in this study may have been affected by some of these inaccuracies. Precise, quantitative estimates for the benthic phosphate fluxes are, therefore, hard to make. However, the purpose of our calculations is to demonstrate regional differences in benthic fluxes in the Arabian Sea and to make some semi-quantitative estimates. In our opinion, the limi-

Table 2

Sediment porosities (top sediment), benthic phosphate fluxes ( $J_p$ ), reactive P accumulation rates ( $A_{\text{Preac}}$ ), reactive P accumulation rates for the top sample ( $A_{\text{Preac}}$  (top)), and the reactive P burial efficiency (PBE), as calculated with Eq. (7). Boxcores located in the OMZ appear in bold

	Porosity	$J_p$ ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ )	$A_{\text{Preac}}$ ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ )	$A_{\text{Preac}}$ (top) ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ )	PBE (%)
BC409	0.75	0.06			
BC411	0.74	0.01			
<b>BC451</b>	<b>0.85</b>	<b>1.76</b>	<b>0.71</b>	<b>0.43</b>	<b>29</b>
BC452	0.76	0.03	0.07	0.08	74
BC453	0.74	0.08	0.12	0.14	60
BC454	0.77	0.14	0.16	0.21	55
<b>BC455</b>	<b>0.85</b>	<b>0.84</b>	<b>0.31</b>	<b>0.25</b>	<b>27</b>
BC458	0.73	0.03	0.07	0.08	72
BC460	0.82	−0.1			
<b>BC463</b>	<b>0.87</b>	<b>0.23</b>	<b>0.23</b>	<b>1.16</b>	<b>49</b>
BC464	0.77	0.09	0.07	0.09	46
BC466	0.73	0.08	0.13	0.15	62
<b>BC484</b>	<b>0.77</b>	<b>6.63</b>			
BC487	0.77	–	0.03	0.05	
BC494	0.75	0.17			
BC497	0.75	0.12			

tations listed above do not seriously hamper such efforts. Possible consequences of the potential inaccuracy of these calculated benthic fluxes will be discussed in later sections.

### 2.3. Solid-phase analysis

The porosity and dry bulk density were calculated from the weight loss on drying at 60°C, assuming a density of 2.65 g cm<sup>-3</sup> for the sediment. For the determination of total solid phase P and Fe, a 250-mg sample was digested in 10 ml of a 6.5:2.5:1 mixture of HClO<sub>4</sub> (60%), HNO<sub>3</sub> (65%) and H<sub>2</sub>O, and 10 ml HF (40%) at 90°C. After evaporation of the solutions at 190°C on a sand bath, the dry residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed by a Perkin Elmer Optima 3000 In-

ductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). All results were checked using international (SO1, SO3) and in-house standards. Relative errors for duplicate measurements are better than 3%. After removal of inorganic carbon with 1 M HCl the organic carbon content (C<sub>org</sub>) was measured on a NA 1500 NCS analyser. Relative errors on duplicate measurements are better than 1%.

The solid-phase speciation of P and Fe in the top 0–2 cm was examined using a five-step sequential extraction scheme (Schenau and De Lange, 2000). Approximately 125 mg of dried and ground sediment was washed with (1) 25 ml 2 M NH<sub>4</sub>Cl, pH = 7 (repeated eight times), (2) 25 ml citrate dithionite buffer (CDB), pH = 8, (3) 25 ml 1 M Na acetate, pH = 4, (4) 25 ml 1 M HCl, and (5) 20 ml HF/HNO<sub>3</sub>/HClO<sub>4</sub> mixture. After extraction steps 2, 3

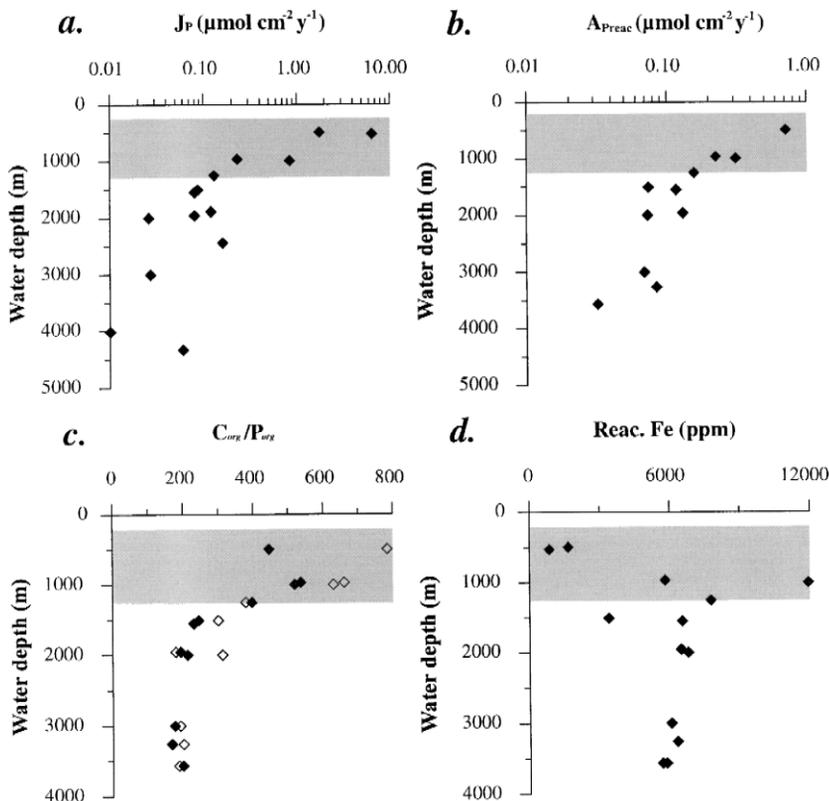


Fig. 3. A plot of (a) benthic phosphate fluxes ( $J_P$ ) vs. water depth, (b) reactive P accumulation rates ( $A_{\text{Preact}}$ ) vs. water depth, (c) sedimentary molar  $C_{\text{org}}/P_{\text{org}}$  ratios vs. water depth for surface samples (0–2 cm;  $\blacklozenge$ ), and samples from the base of each boxcore (25–40 cm;  $\diamond$ ), and (d) reactive iron concentrations ( $\text{Fe}_{\text{CDB}}$ ) in surface sediments (0–2 cm) vs. water depth. The shaded area indicates the position of the OMZ (< 2  $\mu\text{M O}_2$ ).

and 4, the sediment was rinsed with 2 M  $\text{NH}_4\text{Cl}$  and demineralised water to prevent readsorption of phosphate. This extraction scheme is a modification of the SEDEX method developed by Ruttenberg (1992). The application of the 2 M  $\text{NH}_4\text{Cl}$  extraction enables the determination of P associated with biogenic apatite (fish debris; Schenau and De Lange, 2000). The sum of all extraction steps varied between 80% and 90% with respect to the total P concentration. The deficit can be attributed to systematic errors in the measurements of the low P concentrations with ICP-AES. Precision for P was generally better than 5%, except for steps 2 and 3 (10%). Iron oxide contents (reactive iron;  $\text{Fe}_{\text{CDB}}$ ) were determined from the iron concentration extracted in step 2. Some iron associated with AVS may also be extracted during a Na

dithionite extraction (Kostka and Luther, 1994). However, considering the neutral pH (7.8) used here and the fact that no sulphate reduction takes place in these surface sediments (Passier et al., 1997), the contribution of iron associated AVS to  $\text{Fe}_{\text{CDB}}$  is probably negligible. Organic phosphorus ( $\text{P}_{\text{org}}$ ) was determined non-sequentially as the difference between P extractable in 1 M HCl before and after ignition of the sediment (550°C, 2 h; Aspila et al., 1976), and the extracted solutions were analysed with ICP-AES. All measurements were done in duplicate (relative errors smaller than 2%). Precision for samples containing relatively low concentrations of organic P is low (relative errors up to 25%), as it is calculated as the difference between two high concentrations.

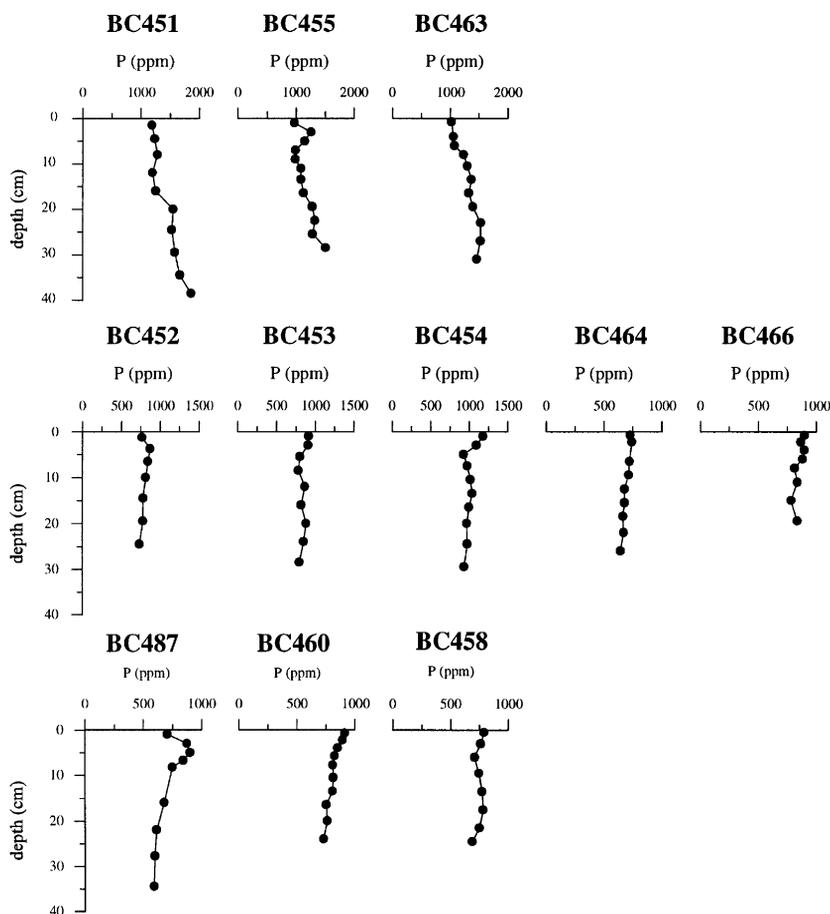


Fig. 4. Solid-phase P profiles for the boxcores used in this study.

### 3. Results

#### 3.1. Porewaters

Interstitial phosphate concentrations increase rapidly with sediment depth to 30–80  $\mu\text{M}$  in sediments located within the present-day OMZ (500–1000 mbss; Fig. 2). In two boxcores (BC451 and BC484), this increase is followed by a decrease with depth. In sediments located below the OMZ (1200–3500 mbss), phosphate concentrations are lower (up to 15  $\mu\text{M}$ ) compared to sediments from 500–1000 mbss, and generally increase only slightly with depth. Porewater ammonium concentrations increase with depth in all boxcores (20–290  $\mu\text{M}$ , not shown). The benthic phosphate fluxes are highest (0.3–6.4  $\mu\text{M cm}^{-2} \text{ year}^{-1}$ ) in sediments located at intermediate water depths (500–1000 m), within the OMZ (Table 2; Fig. 3a). Below 1500-m water depth, benthic phosphate fluxes are lower, varying between 0.01 and 0.3  $\mu\text{M cm}^{-2} \text{ year}^{-1}$ . For one location (BC460), a negative P flux was calculated, which is possibly caused by artifacts introduced during core recovery (e.g., Hensen et al., 1998).

#### 3.2. Solid phase

Organic carbon is enriched in the surface sediments located within the OMZ compared to deep Arabian Basin sediments (Table 1). Total solid-phase P concentrations decrease slightly with sediment depth for sediments located below 1500 mbss (Fig. 4). In contrast, P concentrations increase with sediment depth for sediments located within the OMZ. Accumulation rates of reactive P (i.e., the amount of reactive P removed by burial;  $A_{\text{Preac}}$ ) have been calculated as the product of the mass accumulation rate (Table 1) and the reactive P concentration (being the total solid-phase P concentration minus detrital P concentration) in the lowermost sample of each boxcore. The solid-phase P profiles show that the P concentrations are rather constant with depth in the deepest part of boxcores (Fig. 4). In addition, it is assumed that MARs remained constant for the time period during which the sediments of the boxcores were deposited, as sedimentation rates were constant in the Arabian Sea during the Holocene (Sirocko et al., 1993; Von Rad et al., 1999).  $P_{\text{reac}}$  accumulation rates are highest in the shallowest boxcores (500–1000 m), and decrease with water depth (Fig. 3b).

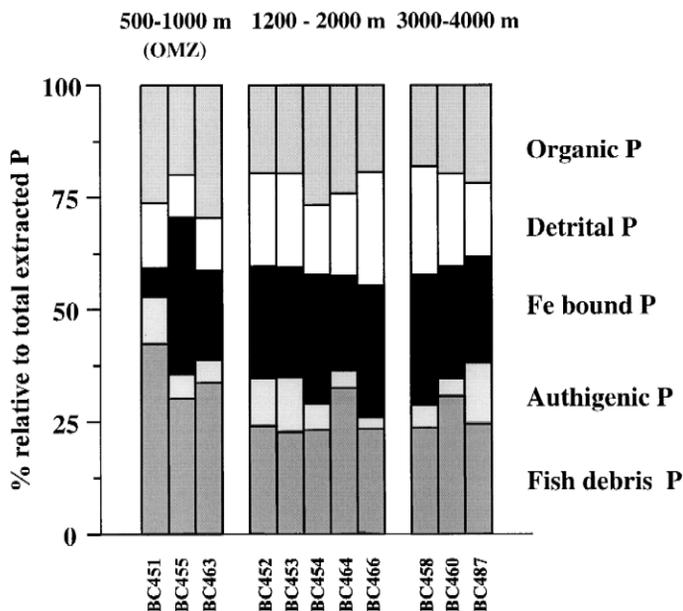


Fig. 5. The solid-phase P speciation relative to total extracted P for the surface sediment samples (0–2 cm) of this study.

This pattern is similar to that observed for the benthic phosphate fluxes vs. water depth (Fig. 3a).

In general, the P speciation of Arabian Sea surface sediments (0–2 cm) does not vary much with water depth (Fig. 5). On average, each of the three major reactive P fractions (organic P, Fe bound P, P associated with fish debris) constitutes ~20–25% of total extracted P. Organic P ( $P_{\text{org}}$ ) and P associated with fish debris ( $P_{\text{fish}}$ ) are enriched relatively to the other P fractions in the sediments located within the OMZ (Fig. 5, Table 3). The iron-bound P fraction ( $P_{\text{Fe}}$ ) is relatively constant (ca. 25%) for sediments below 1200 mbss, but variable for sediments located within the OMZ. Detrital apatite is a relatively more important fraction in the sediments from the deep basin. In all surface sediments, authigenic P contents ( $P_{\text{CFA}}$ ) are low (20–100 ppm). The presence of  $P_{\text{CFA}}$ , however low, may indicate that some authigenic apatite is precipitating, or has been redeposited in these surface sediments. Alternatively, it is possible that the low amounts of extracted  $P_{\text{CFA}}$  can be attributed to partial dissolution of other P fractions, which would imply that no authigenic P phase is present.

Molar  $C_{\text{org}}/P_{\text{org}}$  ratios in the surface sediments (0–2 cm) decrease with water depth from 400 to 500 at 500 mbss to 200 at 2000 mbss (Fig. 3c). Below this water depth,  $C_{\text{org}}/P_{\text{org}}$  ratios remain fairly constant. For OMZ sediments molar  $C_{\text{org}}/P_{\text{org}}$  ratios are higher for deeper samples (25–40 cm), indicating ongoing preferential loss of P relative to carbon upon burial. In contrast, molar  $C_{\text{org}}/P_{\text{org}}$  ratios remain

constant with sediment depth for the deep pelagic sites. Dithionite-extractable (reactive) iron concentrations are constant in surface sediments below the OMZ (~6000 ppm; Fig. 3d). Around the base of the present-day OMZ, sedimentary reactive iron is enriched in two boxcores (BC455 and BC454), while sediments from around 500 m water depth are depleted in reactive Fe. Molar Fe/P ratios in the dithionite-extractable fraction vary between 16 and 23 for all samples.

## 4. Discussion

### 4.1. Benthic phosphate release

The pattern of benthic P release with water depth in the Arabian Sea (Fig. 3a) is similar to that observed along the continental margins of California (Ingall and Jahnke, 1994; McManus et al., 1997), and the Southern Atlantic (Zabel et al., 1998; Hensen et al., 1998). These studies report benthic phosphate fluxes of a same magnitude as presented here (0–10  $\mu\text{M cm}^{-2} \text{ year}^{-1}$ ). For the oxic sediments deposited below the OMZ, the low benthic phosphate fluxes concur with a slight decrease in solid-phase P concentrations with sediment depth. However, for the OMZ sediments, where the benthic P fluxes are highest, solid-phase P concentrations increase with sediments' depth (Fig. 4). Furthermore, a comparison between the benthic phosphate fluxes and the phosphorus accumulation rates for the top of these sediments ( $A_{\text{preac}}$  (top)) indicates that even if all solid-phase P in the top of the sediment were mobilized, insufficient reactive P is present to explain the observed benthic phosphate flux (Table 2). This discrepancy between the solid-phase P profiles and the estimated benthic fluxes is best explained by a rapid regeneration of particulate P shortly after deposition. When reactive P is mobilized rapidly, it will not be detected as a distinct decrease of a solid-phase P fraction in the top of the sediment. However, in order to produce the high subsurface phosphate concentrations some downward mixing of reactive P into the sediment is necessary (Schenau et al., 2000). For OMZ sediments bioturbation is reduced, but some mixing of the upper sediments does occur (Jannink et al., 1998; Smith et al., 2000). The increase of solid-phase P with sediment depth for

Table 3  
Solid-phase phosphorus phases for the surface sediment samples (0–2 cm) of this study (ppm)

	$P_{\text{fish}}$ (ppm)	$P_{\text{Fe}}$ (ppm)	$P_{\text{CFA}}$ (ppm)	$P_{\text{det}}$ (ppm)	$P_{\text{org}}$ (ppm)
<b>BC451</b>	<b>382</b>	<b>58</b>	<b>96</b>	<b>131</b>	<b>237</b>
BC452	158	164	70	136	130
BC453	157	170	85	145	138
BC454	189	235	48	127	219
<b>BC455</b>	<b>320</b>	<b>372</b>	<b>57</b>	<b>98</b>	<b>213</b>
BC458	145	179	31	147	112
BC460	205	167	26	137	133
<b>BC463</b>	<b>310</b>	<b>184</b>	<b>47</b>	<b>108</b>	<b>273</b>
BC464	179	116	21	101	133
BC466	143	179	58	153	119
BC487	194	188	106	128	173

OMZ sediments is related to the precipitation of an authigenic apatite phase (Schenau et al., 2000).

Benthic phosphate fluxes are thus regulated by diagenetic regeneration processes occurring briefly after deposition. As a consequence, the P speciation of the surface sediments can only be used as a qualitative indicator for the contribution of each individual reactive P source. In Sections 4.1.1, 4.1.2 and 4.1.3, the relative contributions of the three principal sources of reactive P to the high benthic phosphate fluxes in sediments of the OMZ will be assessed, namely (1) organic matter, (2) iron oxides, and (3) fish debris.

#### 4.1.1. Organic matter degradation

Deposition of organic matter is quantitatively the most important mode by which reactive P is transferred to sediments (Froelich et al., 1982; Delaney, 1998). Burial of organic P, however, is not the foremost reactive P sink in most marine environments (Filippelli and Delaney, 1996; Delaney, 1998). This also holds for Arabian Sea sediments, as is indicated by the solid-phase P speciation (Fig. 5). Sediment trap studies have shown that ca. 90% of the export flux ( $\sim 40 \text{ gC m}^{-2} \text{ year}^{-1}$ ) is recycled in the water column (Eppley, 1989; Lee et al., 1998). Accordingly, the potential flux of organic P arriving at the sediment surface is  $\sim 0.3 \mu\text{mol P cm}^{-2} \text{ year}^{-1}$  (assuming a Redfield nutrient ratio). Lateral transport may supply an additional input of organic material in margin sediments (Jahnke et al., 1990).

There is a good correlation between the benthic phosphate flux and the  $P_{\text{org}}$  accumulation rate (top

cm) (Fig. 6a), suggesting that the high benthic phosphate fluxes in these sediments may be linked to organic matter decomposition. Phosphate release from organic matter decomposition for sediments located within the OMZ (BC451, BC455, BC463, BC484) can be estimated from ammonium porewater concentrations (Froelich et al., 1988; Ruttenger and Berner, 1993; Schuffert et al., 1994; McManus et al., 1997). An empirical fit was made to the ammonium porewater profiles, using the equation (Berner, 1980):

$$C = C_0 + \alpha_1(1 - e^{-\alpha_2 x}) \quad (4)$$

where  $C$  and  $C_0$  are the concentrations of ammonium at depth  $x$  and 0 (cm), respectively, and  $\alpha_1$  and  $\alpha_2$  empirical constants. Considering the suboxic nature of these sediments, oxidation of ammonium can be neglected. Assuming that organic matter has a Redfield nutrient ratio (C/N/P, 106:16:1), and is decomposing stoichiometrically (i.e.,  $\alpha_2$  for ammonium equals  $\alpha_2$  for phosphate), the empirical constants  $\alpha_1$  for phosphate ( $\alpha_{1P}$ ) can be calculated with (Schuffert et al., 1994):

$$\alpha_{1P} = \alpha_{1N} \times D_N / 16 \times D_P \quad (5)$$

where  $D_N$  and  $D_P$  are the whole diffusion coefficient constants for ammonium and phosphate, respectively, corrected for the in-situ bottom water temperature (Li and Gregory, 1974). Possible contributions of the more refractory terrestrial organic P can be neglected, as accumulating organic matter in the sediments of the Arabian Sea is predominantly of a marine origin (Pedersen et al., 1992; Van der Weijden et al., 1999). The values for  $\alpha_{1P}$  and  $\alpha_2$

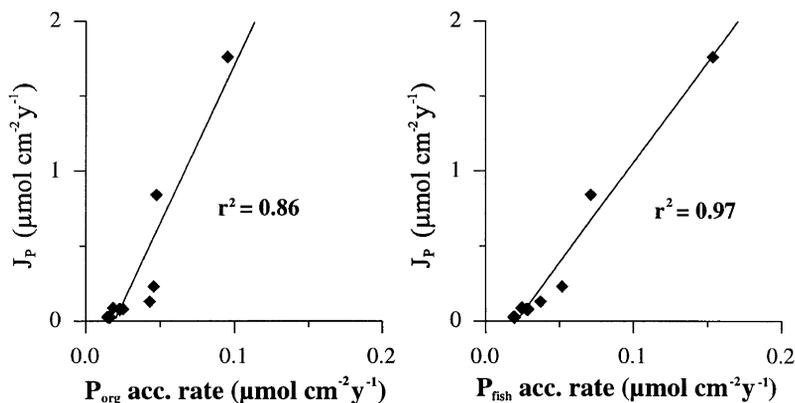


Fig. 6. A plot of the benthic P flux ( $J_p$ ; Table 1) vs. (a) the  $P_{\text{org}}$  accumulation rate and (b) the  $P_{\text{fish}}$  accumulation rate, respectively.

were inserted in Eq. (4) and used to plot the theoretical phosphate profile resulting from organic matter degradation alone, i.e. in absence of iron redox cycling, fish debris dissolution and authigenic apatite precipitation (Fig. 2; Schuffert et al., 1994). Subsequently, the maximum benthic flux resulting from organic matter decay ( $J_{\text{Porg}}$ ) was calculated from the linear phosphate gradient in the upper part of the sediment in the modelled phosphate profiles using Eqs. (1) and (2) (Table 4). The calculated  $J_{\text{Porg}}$  fluxes (0.16–0.20  $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ ) are close to the organic P deposition flux of 0.3  $\mu\text{mol cm}^{-2} \text{ year}^{-1}$  estimated at the beginning of this section, indicating that most organic P is recycled during early diagenesis. A comparison between the calculated  $J_{\text{Porg}}$  fluxes and the benthic phosphate fluxes ( $J_{\text{P}}$ ), however, indicates that organic matter degradation in OMZ sediments produces insufficient phosphate (3–70%) to explain the high benthic phosphate fluxes.

The  $C_{\text{org}}/P_{\text{org}}$  ratio for surface sediments (0–2 cm) located within the OMZ are higher than the Redfield ratio of organic matter (106), which can be attributed to preferential loss of P relative to carbon during organic matter degradation. As a large fraction of the organic matter arriving at the sediment water interface is remineralised within a few months

or years (e.g., Eppley, 1989), preferential release of P probably occurs soon after deposition. The calculated P fluxes originating from organic matter decomposition ( $J_{\text{Porg}}$ ) may thus have been underestimated. Assuming that approximately two thirds of the organic matter is rapidly decomposed after deposition (Reichert, 1998) during which the  $C_{\text{org}}/P_{\text{org}}$  ratio increases from 106 to 500, it follows that  $C/P$  of the regenerated organic matter equals 75. As the result of preferential P release, the calculated  $J_{\text{Porg}}$  fluxes may thus increase by a factor of at most 1.4. This is still insufficient to explain the observed benthic phosphate fluxes (with exception of BC463, Table 4).

We conclude that the high benthic phosphate fluxes in sediments located within oxygen depleted bottom waters can only partially be explained by high rates of sedimentary organic matter degradation and preferential P release. This finding is consistent with other studies concerning P cycling in continental margin sediments underlying low BWO concentrations (Froelich et al., 1988; Van Cappellen and Berner, 1988; Heggie et al., 1990; Schuffert et al., 1994).

#### 4.1.2. Phosphate desorption from iron oxides

A second potential carrier of reactive P to the sediment is iron (hydr)oxide, which is deposited as a detrital mineral and as surface coating on sedimentary particles (e.g., Berner, 1973; Froelich et al., 1988). After burial in the suboxic zone of the sediment, iron oxides start to dissolve and the adsorbed phosphate is released into the interstitial waters. In view of the low oxygen concentrations in the intermediate water column, it is questionable whether the accumulation of iron oxides may transfer reactive P to sediments residing in the OMZ. Surface sediments from 500 mbss are characterized by an absence of reactive iron (Fig. 3d), indicating that iron oxides have already been reduced in the water column or at the sediment water interface. In contrast, sediments located near the lower boundary of the OMZ (1000–1250 mbss) have relative high concentrations of reactive iron. Bottom water oxygen concentrations are somewhat higher here, allowing the deposition of iron oxides. As the oxic–suboxic interface is located close to the sediment surface (Van der Weijden et al., 1999), reactive iron becomes enriched due to

Table 4

Calculated P fluxes for the box cores located within the oxygen minimum zone (BC484, BC451, BC455, BC463). First column: benthic P fluxes ( $J_{\text{P}}$ ) as estimated from the porewater phosphate profiles; Second column: the estimated benthic P flux as the result of organic matter degradation ( $J_{\text{Porg}}$ ), calculated from the ammonium porewater profiles assuming stoichiometric organic matter degradation according to a Redfield nutrient ratio (C/N/P 106:16:1; see text); Third column: potential input of P associated with reducible iron hydroxides, as calculated with Eq. (6) ( $J_{\text{PFe}}$ ; see text); Fourth column: the potential input of P associated with fish debris ( $J_{\text{Pfish}}$ ), calculated from the fish production in the Arabian sea (see text)

	$J_{\text{P}}$ ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ )	$J_{\text{Porg}}$ ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ )	$J_{\text{PFe}}$ ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ )	$J_{\text{Pfish}}$ ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ )
BC451	1.76	0.16	0.07	0.7
BC455	0.84	0.18	0.04	0.7
BC463	0.23	0.17	0.03	0.4
BC484	6.63	0.20	0.02	“not determined”

reprecipitation of upward diffusing  $\text{Fe}^{2+}$ , mobilized in the suboxic part of the sediment.

The primary supply of P associated with reducible iron hydroxides ( $J_{\text{PF}_e}$ ,  $\mu\text{mol P cm}^{-2} \text{ year}^{-1}$ ) can be estimated with the equation (after Ingall and Jahnke, 1997):

$$J_{\text{PF}_e} = \frac{\text{Fe}_{\text{CDB}} \times \text{MAR}}{(\text{Fe}/\text{P})_{\text{red}} \times 55,800} \quad (6)$$

where  $\text{Fe}_{\text{CDB}}$  is the concentration of iron oxides in the surface sediment (ppm), MAR the mass accumulation rate ( $\text{g cm}^{-2} \text{ ka}^{-1}$ , Table 1), and  $(\text{Fe}/\text{P})_{\text{red}}$  the molar ratio of adsorbed phosphate in newly deposited reducible iron particles. The  $\text{Fe}_{\text{CDB}}$  concentrations in surface sediments within the OMZ, however, cannot be used to quantify the  $J_{\text{PF}_e}$  flux, because iron oxides may already have been partly reduced at the sediment water interface, or have become enriched due to diagenetic iron cycling. Therefore, an estimate for the  $J_{\text{PF}_e}$  flux was made based on the  $\text{Fe}_{\text{CDB}}$  concentrations recorded in the surface sediments located below the OMZ, which have probably not been subjected to significant diagenetic changes. These rather constant  $\text{Fe}_{\text{CDB}}$  concentrations ( $\sim 6000$  ppm), suggest that accumulation of iron oxides is directly proportional to the sediment accumulation rate. Previous estimates for the molar  $(\text{Fe}/\text{P})_{\text{red}}$  ratio for newly buried iron oxides range from 20 to 26 (Lucotte et al., 1994; Louchouart et al., 1997; Anschutz et al., 1998), which correspond with  $(\text{Fe}/\text{P})_{\text{red}}$  ratios of 20 observed in the surface sediments of this study. The  $J_{\text{PF}_e}$  fluxes thus calculated for the boxcores located within the OMZ range from 0.02 to 0.07  $\mu\text{mol cm}^{-2} \text{ year}^{-1}$  (Table 4). These fluxes are maximum values, as it is assumed that no reduction of iron oxides occurs during their transit through the OMZ. Even so, deposition and subsequent reduction of iron oxides significantly may contribute only 4 to at most 10% to the benthic phosphate fluxes in the continental margin sediments (Table 4). Van Cappellen and Berner (1988) and Ingall and Jahnke (1997) arrived at the same conclusion for continental margin sediments underlying low oxygenated bottom waters offshore California.

#### 4.1.3. Fish debris dissolution

The hard parts of fish (scales, bones, teeth) consist for 60–70% of hydroxyapatite (e.g., Posner et

al., 1984). Seawater is undersaturated with respect to biogenous apatite (Atlas and Pytkowicz, 1977), and, as a result, fish debris undergo dissolution in the water column and during early diagenesis. Accumulation of fish debris has been recognized as a potentially important process to add reactive P to marine sediments (Suess, 1981; Van Cappellen and Berner, 1988). There are few studies which consider dissolution of fish debris as a potential source for interstitial phosphate, which is probably due to the fact that (until now) they were not chemically distinguishable from other P fractions.

The high biomass of phyto- and zooplankton in the Arabian Sea leads to high rates of fish production (e.g., FAO, 1981). Based on the trophic–dynamic model of Iverson (1990), we have estimated a present-day fish production for the Pakistan Margin and the central Arabian Sea of 23.8 and 14.0  $\text{g m}^{-2} \text{ year}^{-1}$ , respectively (wet weight; for details, see Schenau and De Lange, 2000). Assuming a phosphorus dry weight fraction of marine fish of 0.03 (Anonymous, 1982), and a ratio of fish wet wt.% to fish dry wt.% of 3.3 (Iverson, 1990), the potential production of P associated with biogenic apatite varies between 0.7 and 0.4  $\mu\text{mol P cm}^{-2} \text{ year}^{-1}$  (Table 4). This calculation gives only a rough estimate for the potential  $\text{P}_{\text{fish}}$  export flux ( $J_{\text{Pfish}}$ ), but provides a reasonable order of magnitude. This potential export flux of P associated with fish bones is approximately a factor 4–8 less than that of organic P. Fish bone particles, however, are relatively large and have a high density compared to seawater, which will make them sink relatively fast to the sea floor. It is therefore plausible that dissolution of fish debris predominantly occurs after deposition. In addition, fish debris may be advected by lateral transport. Accumulation of fish debris may thus potentially transfer a significant quantity of reactive P to the sediments of the Arabian Sea.

Application of the  $\text{NH}_4\text{Cl}$  extraction enables, for the first time, an evaluation of fish debris accumulation in marine sediments in relation to the other reactive P fractions. In the surface sediments of the Arabian Sea,  $\text{P}_{\text{fish}}$  is an important reactive P fraction (Fig. 5). Particularly sediments located within the OMZ have relatively high  $\text{P}_{\text{fish}}$  concentrations. The high accumulation rate of fish debris in these continental slope sediments can be attributed to high fish

production rates in the surface waters and reduced biogenic apatite dissolution rates in the water column in comparison to the deep Arabian Basin (Schenau and De Lange, 2000). The  $P_{\text{fish}}$  accumulation rate (top cm) correlates well with the benthic phosphate flux ( $r^2 = 0.97$ ; Fig. 6b), suggesting that fish debris may be an important source for phosphate generation from these sediments. The calculated  $P_{\text{fish}}$  accumulation rate (top cm) is only 10% of the benthic P flux, which is likely to be caused by most fish debris dissolving shortly after their deposition (see Section 4.1).

Based on (a) the good correlation between the benthic phosphate fluxes and the  $P_{\text{fish}}$  accumulation rates, (b) the potentially high accumulation rate of fish debris in the Arabian Sea, and (c) the insufficient contribution of other reactive P sources (organic matter and iron oxides), we argue that the high benthic phosphate fluxes in continental margin sediments of the Arabian Sea are to a large extent the result of sedimentary fish debris dissolution. This finding may have important implications for our understanding of the oceanic P cycle. Firstly, processes governing the dissolution and preservation of fish debris may control benthic P regeneration in many marine environments. Secondly, fish debris dissolution may drive CFA formation in sediments underlying areas of high productivity, as has previously been suggested by Suess (1981), thereby regulating P burial.

#### 4.2. Phosphorus burial in the Arabian Sea

To evaluate regeneration and burial of P in sediments of the Arabian Sea, reactive P burial efficiencies (PBE) have been calculated using the equation (after Ingall and Jahnke, 1994):

$$\text{PBE (\%)} = 100 \times A_{\text{Preac}} / (J_{\text{P}} + A_{\text{Preac}}) \quad (7)$$

where  $A_{\text{Preac}}$  is the accumulation rate of reactive P and  $J_{\text{P}}$  the benthic phosphate flux (Table 2). The P burial efficiencies are lowest for the sediments located within the OMZ (BC451, BC455 and BC463) and increase with water depth (Fig. 7; Table 2). These results compare favourably with a similar study by Ingall and Jahnke (1994). There is a relatively large error in the PBE due to uncertainties in the benthic phosphate fluxes. However, the signifi-

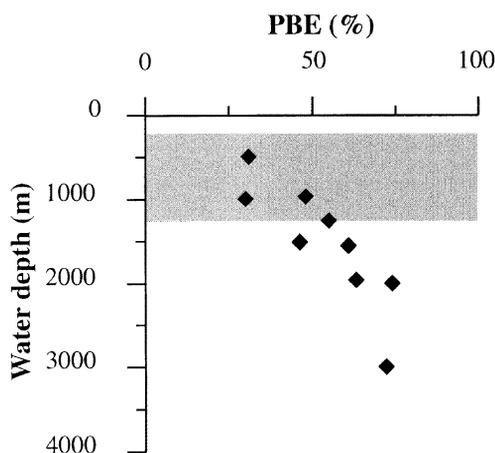


Fig. 7. A plot of the P burial efficiencies (PBE) vs. water depth (%). The shaded area indicates the of the position of the OMZ ( $< 2 \mu\text{M O}_2$ ).

cantly larger differences in benthic phosphate fluxes as compared to differences in P accumulation rates (Table 2) validates the conclusion that the PBE is lower for OMZ sediments than for those in the deep Arabian Basin.

The relatively low P burial efficiencies calculated for OMZ sediments seem to contrast with their high  $P_{\text{reac}}$  accumulation rates. Excluding the coastal upwelling area off Oman, primary productivity rates are similar throughout the northern Arabian Sea (Qasim, 1982; Banse, 1987; Van der Weijden et al., 1999). The difference in surface water productivity and export production between the Pakistan coastal area and the open ocean region is probably less than a factor two (Qasim, 1982; Brock et al., 1994; Pollehne et al., 1993). Accordingly, the vertical particulate P flux leaving the photic zone in these two areas, i.e. the export P flux, is of the same order of magnitude. The  $P_{\text{reac}}$  accumulation rates on the continental margin, however, are 5 to 20 times higher than in the deep Arabian Basin (Table 2). This would imply that sedimentary P retention relative to the export-P fluxes (from hereon Export Phosphorus Retention, EPR) is more efficient in shallow, continental slope sediments located within the OMZ. How can this observation be in accordance with the observed pattern of P burial efficiencies (Fig. 7) and the commonly held view that P regeneration is more efficient under oxygen depleted bottom water conditions?

Low sedimentary PBEs under oxygen depleted bottom water conditions have been attributed to less efficient phosphate cycling associated with iron oxides, or redox-dependent P cycling of benthic microorganisms (Ingall and Jahnke, 1994, 1997). However, we argue that the water depth related variations in PBE observed in the Arabian Sea (Fig. 7) may also be related to differences in the reactivity of the particulate P flux arriving at the sediment. The P deposition rates (i.e., the sum of the  $P_{\text{reac}}$  accumulation rates and benthic phosphate fluxes) in the Arabian Sea decrease with water depth (Fig. 3a,b). This is confirmed by sediment trap studies that show a large reduction in the vertical organic matter flux, the prime carrier of P, in the upper 1000 m of the water column (Lee et al., 1998). As a large fraction of reactive P is remobilised with increasing water depth, the nature of the remaining P becomes more refractory, and, as a consequence, relatively less phosphate regeneration may take place in the sediment. Absence of significant P mobilisation after burial in the deep basin sediments is demonstrated

by the low interstitial phosphate concentrations (Fig. 2) and the constant  $C_{\text{org}}/P_{\text{org}}$  ratio with sediment depth (Fig. 3c). In contrast, more shallow sediments receive a relative much higher input of reactive P, which will cause higher rates of sedimentary phosphate regeneration, and thus lower sedimentary P burial efficiencies. In addition, lateral transport from continental slope and shelf areas may result in redeposition of reworked organic material in margin sediments (Jahnke et al., 1990). The input of a more reactive or refractory P fraction (organic P, fish debris, resuspended authigenic apatite) will affect the burial efficiency.

Sedimentary phosphorus burial efficiencies, thus, should be interpreted with caution in terms of the environmental conditions, since the degree of P mobilisation in sediments and subsequent release to the bottom water is to a large extent dependent on the differences in P regeneration occurring in the water column and redeposition processes. This is illustrated in Fig. 8 for two boxcore sites on the Pakistan continental Margin (BC451 and BC452). The export

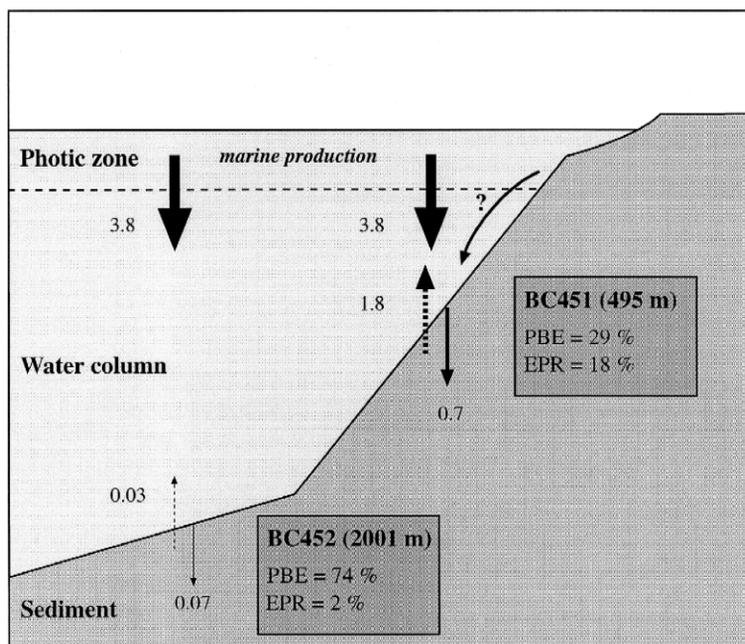


Fig. 8. Schematic representation of phosphorus fluxes ( $\mu\text{mol cm}^{-2} \text{ year}^{-1}$ ) for a shallow (BC451, 495 m) and a deep pelagic site (BC452, 2001 m) on the continental slope of Pakistan. Export productivity and, therefore, the export flux of particulate phosphorus will approximately be the same, as these two sites are located in close proximity to each other (ca.  $3.8 \mu\text{mol cm}^{-2} \text{ year}^{-1}$ ). Lateral transport may provide an additional input of reactive P in boxcore 451. Although the phosphorus burial efficiency (PBE) is lower for BC451, export phosphorus retention (EPR) in the sediment is higher.

flux of particulate P (i.e.,  $\sim 3.1 \mu\text{mol P}_{\text{org}} \text{cm}^{-2} \text{year}^{-1} + \sim 0.7 \mu\text{mol P}_{\text{fish}} \text{cm}^{-2} \text{year}^{-1}$ ) will be approximately similar, as the sites of these boxcores are located in relatively close proximity to each other (Fig. 1). As discussed, the sedimentary burial efficiency for BC451 (495 mbss) is higher than for BC452 (2000 mbss) (Fig. 7). The export phosphorus retention for BC451, however, is much higher, as relatively less P remobilisation takes place in the water column. The high phosphorus retention for BC451 may partly be explained by the input of reworked material from the continental shelf an slope. A study on the nature of the organic matter deposited in the boxcores of this study indicated, however, that lateral transport plays only a minor role (Van der Weijden et al., 1999). Consequently, the PBE values presented in this study do not reflect the total sedimentary P retention relative to the P produced in upper water column.

The export P retention is higher in continental margin sediments of the Arabian Sea, which are located within the OMZ compared to deep basin sediments. This more efficient P removal can be attributed to several processes, namely (a) shallower water depths, resulting in higher deposition rates of reactive P, (b) more rapid burial of P as the result of higher sediment accumulation rates, (c) low BWO concentrations which may enhance the preservation of organic matter (e.g., Demaison and Moore, 1980; Canfield, 1993) and of fish debris (Schenau and De Lange, 2000), and d) high rates of phosphogenesis, induced by high interstitial phosphate concentrations (Schenau et al., 2000). In view of all variables involved, sedimentary burial efficiencies presented in this study cannot be used to resolve the role of bottom water redox conditions on sedimentary P cycling. If this is to be done, phosphorus burial efficiencies should be compared from sample sites with similar water depths, sedimentation rates and primary productivity rates, but contrasting redox conditions.

## 5. Conclusions

In the Arabian Sea, benthic phosphate fluxes are highest on the continental slope, underlying low bottom water oxygen concentrations. Reactive P re-

generation in these sediments occurs briefly after deposition. Organic matter degradation and phosphate desorption from iron oxides provide insufficient phosphate to explain the high benthic phosphate fluxes. The good correlation between benthic phosphate fluxes and accumulation rates of P associated with fish debris in surface sediments, and the potentially high accumulation rate of fish debris in the Arabian Sea suggest that dissolution of biogenic apatite contributes a significant proportion of the benthic phosphate regeneration in these sediments. Factors governing dissolution and preservation of fish debris thus may play an important role in the burial and regeneration of P in continental margin sediments.

The burial efficiency of phosphorus, calculated from the accumulation rates of reactive phosphorus and the benthic phosphate fluxes, is lower for continental margin sediments located within oxygen depleted bottom waters. However, primary productivity rates and, therefore, the export flux of particulate P are similar throughout the northern Arabian Sea. Accordingly, P removal by burial is more efficient in the relatively shallow continental slope sediments located within the oxygen minimum zone in comparison to deep basin sediments. The effectiveness of P burial is to a large extent regulated by P regeneration occurring in the water column and redeposition processes. Sedimentary phosphorus burial efficiencies, thus, should be interpreted with caution.

## Acknowledgements

We want to thank W.J.M. van der Linden and C.H. van der Weijden, who were the chief scientists on the NIOP cruises during the 1992–1993 Netherlands Indian Ocean Programme. Helen de Waard, and Gijs Nobbe are also thanked for their contribution to the laboratory analyses. Hilde Passier is acknowledged for providing the porewater data of BC484 and BC487. Critical reviews by C.H. van der Weijden, I.A. Nijenhuis, A. Rutten, Dr. D.J. Burdige, Dr. P. Anschutz and an anonymous reviewer significantly improved this manuscript. This research was funded by the Netherlands Organization for Scientific Research (NWO).

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