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Solid phase phosphorus species and preservation of fish remains in marine sediments of areas of high primary productivity and oxygen seasonality (36°S, central South Chile)

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The main input of phosphorus to the ocean is associated with river runoff, while this element leaves the marine system via burial in the sediments. Solid phase P accumulation is a function of bottom water and surface sediment oxygenation. Theory predicts that suboxic/anoxic sediments act as a source of phosphate, which is released from organic matter and iron oxides, while authigenic precipitation and biogenic apatite preservation are both favored in a phosphate saturated environment. In this paper, we present the results of solid phase phosphorus speciation in sediments collected in central south Chile on the continental shelf off Concepción. This area is characterized by very high biological productivity and the formation of a strong oxygen minimum zone during summer. We found that total solid phase P was dominated by inorganic phases (60%), mostly comprised by iron-bound P and biogenic apatite P. As expected, biogenic apatite P and iron-bound P were negatively correlated and reflected bottom water oxygen fluctuations during the period analyzed (February–September 2009). The biogenic apatite (fish debris) preservation potential was negatively correlated with bottom water dissolved oxygen and its burial averaged 16% of water column's fish production estimated with a trophic dynamic-model that included SeaWIFS-MODIS satellite primary productivity estimations. In spite of intrusions of oxygen in the water column evidenced by the thinning of the oxygen minimum layer in autumn-winter, bottom waters remained suboxic during the studied period and appear to have favored biogenic apatite P (P_{fish}) preservation. This finding supports the potential of P_{fish} as a paleotracer for fish abundance in areas previously not considered because of the lack of laminated sediments.

Keywords: fish debris, biogenic apatite, seasonal coastal upwelling, hypoxia, central-south Chile

INTRODUCTION

River runoff is the main source of phosphorus (P) to oceanic waters, while the main sink is sediment burial, and because P cannot be fixed from the atmosphere, it is considered the ultimate limiting macronutrient for water column primary production over geological time scales (Paytan and McLaughlin, 2007). Sedimentary (solid phase) P is present in minerals, such as biogenic hydroxyapatite (e.g., P_{fish}, Schenau and De Lange, 2000), iron-bound P (P–Fe), detrital-P (e.g., fluorapatite carbonates), and organic P (Ruttenberg, 1992; Slomp *et al*., 1996). In the sediments, the non-refractory fraction of organic matter is decomposed, releasing phosphate to pore waters and the water column. Phosphorus released from the inorganic phase in marine sediments is governed by changes in redox conditions. Thus, when the water column is predominantly oxic, phosphate is adsorbed onto iron oxides (Slomp *et al*., 1996), whereas when reducing conditions prevail in surface sediments, phosphate is released from iron oxides favoring the formation of insoluble authigenic minerals (i.e., authigenic hydroxyapatite) permanently removing P from the water column (Slomp *et al*., 1996). Although it is usually assumed that phosphorus transformation at the sediment water interface and in surface sediments is an abiotic process, recent evidence suggests that prokaryotes and certain eukaryotes such as the yeast *Candida maltosa*, are capable of remineralizing recalcitrant organophosphorus compounds such as phosphonates. Moreover, microbes can also contribute to the formation of recalcitrant organic compounds and biogenic apatite and thus can ultimately contribute to P burial in sediments (Paytan and McLaughlin, 2007). The mechanisms of P sequestration by bacteria in the sediment are not still clear but it has been suggested that bacteria apatite formation is a significant phosphorus sink under anoxic bottom water conditions in the Namibian upwelling system where modern phosphorite formation is occurring associated with

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bacteria *Thiomargarita* and *Beggiatoa* (e.g., Goldhammer *et al.*, 2010, 2011).

Phosphorus burial in open ocean marine sediments ranges between 9.3 and 34 × 10^{10} mol yr^{-1} and mostly consists of reactive P (i.e., organic P, P–Fe, loosely sorbed P such as biogenic apatite-, and authigenic P), whereas the nonreactive component is associated with terrigenous material (Paytan and McLaughlin, 2007). According to several studies, the sedimentary P sink is comprised of ~3.2 × 10^{10} mol yr^{-1} of authigenic apatite and a similar flux of organic P. However, such figures are highly uncertain and other studies suggest that authigenic apatite fluxes could be as high as 8–9 × 10^{10} mol yr^{-1} while iron-bound/adsorbed P flux could reach values up to 5 × 10^{10} mol yr^{-1} (Paytan and McLaughlin, 2007 and references therein). Despite uncertainties, it is clear that major sedimentary sinks for reactive phosphorus in the marine system are authigenic apatite (~50%), Fe–P (~25%), and organic P (~25%) (Slomp and Van Cappellen, 2007 and references therein). Although biogenic apatite, the mineral constituent of vertebrate skeletons such as fish, is considered a minor sink (Froelich *et al.*, 1982; Slomp and Van Cappellen, 2007), it may be important in upwelling areas such as the Peru–Chile margin (Suess, 1981), which is characterized by very high fish production (Fréon *et al.*, 2009). Preservation of fish remains depends on sedimentation rate (related to fish productivity in the water column), water depth, and oxygen concentration in bottom waters (Schenau and De Lange, 2000). Scales and bones deposited in laminated sediments under anoxic conditions in the Santa Barbara Basin in the California Current System were first used as proxies for fish productivity (Soutar and Isaacs, 1969, 1974; Baugartner *et al.*, 1992). Reconstructions of water column fish abundance have been attempted using sediments collected from the shelf and the upper shelf break of the Peru–Chile Current System off central Peru and northern Chile (Devries and Pearcy, 1982; Schwartzlose *et al.*, 1999; Valdés *et al.*, 2008; Salvatteci *et al.*, 2012) and in the Benguela Upwelling System (Shackleton, 1987; Struck *et al.*, 2002). Other potentially suitable areas for fish abundance reconstructions pose certain challenges. For instance, in the Saanich Inlet in the California Current System, scale recovery can be poor and preservation issues can be significant depending on the degree of lamination of the sediments and the ecology (e.g., predation rates) of the fish community (O'connell and Tunnicliffe, 2001). In several oxygen poor areas (suboxic), fish scales are frequently too fragmented for identification to species level. However, in these areas the high occurrence of remains and bone fragments demonstrates that biogenic apatite does not completely dissolve and can be used as a proxy for fish productivity (O'connell and Tunnicliffe, 2001).

For instance, off Callao (Peru–Chile Current System) the analysis of a sediment core dated with ^{210}Pb and ^{14}C revealed an interval between the late 13th century and the mid-19th century when the strength of the oxygen minimum zone (OMZ) appears to have weakened (Díaz-Ochoa *et al.*, 2009). Concomitantly, fish scale recovery during this interval was minimal (Díaz-Ochoa *et al.*, 2009), similar to what has been recently reported for the area off Pisco in Peru (Sifeddine *et al.*, 2008; Salvatteci *et al.*, 2012). Despite the alteration of fish scale integrity by the fluctuation in OMZ strength, which makes species specific paleo-reconstructions difficult (Emeis *et al.*, 2010), the affected sediment horizons may still contain fragmented scales and bones (Díaz-Ochoa *et al.*, 2008, 2009) that can be used as proxies for the abundance of fish communities inhabiting the water column.

In this paper we assess the importance of fish debris (biogenic hydroxyapatite) preservation in the highly biologically productive upwelling area off Concepción in central Chile to assess the potential of phosphorus contained in fish remains as a proxy for fish abundance as a function of seasonal oscillations in bottom water oxygenation. The upwelling area off Concepción is one of the most productive regions for fisheries and the possibility of assembling new proxy records for fish abundance within the southern-most extension of the Peru–Chile current will help to better understand long term fish population dynamics in this region. This study might also help to incorporate new settings traditionally not used in paleo reconstructions of fish populations because of the absence of laminated sediments.

Material and Methods

Study area

The hydrography of central Chile is dominated by the Peru Chile Current flowing northward and transporting Subantarctic waters between 0 and 100 m depth. Below the Peru Chile Current, the poleward Gunther Undercurrent carries oxygen-depleted equatorial subsurface water between 100 and 400 m depth (Shaffer *et al.*, 1995; Strub *et al.*, 1998). Primary productivity levels in the upwelling area off central Chile are amongst the highest of the world ocean with ~1 ± 0.2 kg C m^{-2} yr^{-1} (Daneri *et al.*, 2000; Montero *et al.*, 2007). On the shelf, at ~36°S, the zonal extension of the Eastern South Pacific OMZ is reduced to a thin band (maximal thickness <50 m), whereas its upper limit becomes shallower towards the coast (Fuenzalida *et al.*, 2009). The OMZ off central Chile exhibits a formation-destruction cycle between spring and fall (Paulmier *et al.*, 2006). Water column oxygen fluctuates widely at the seasonal scale from <10 μM in summer to >100 μM in fall–winter off Concepción (Graco *et al.*, 2001; Paulmier *et al.*, 2006). The OMZ also shows vari-

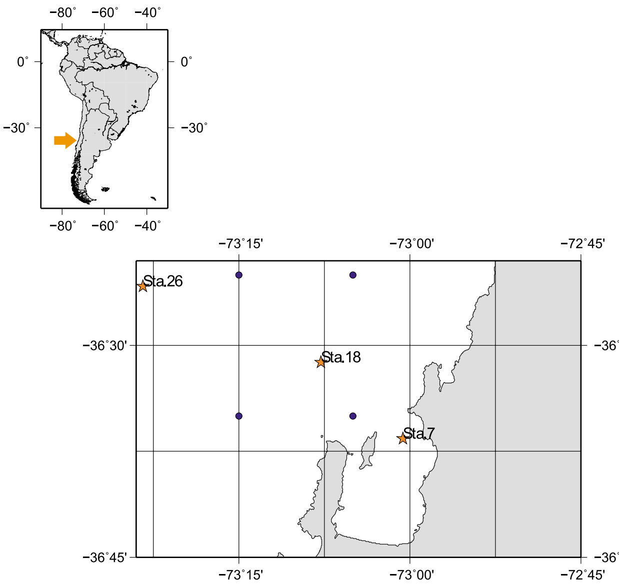

Fig. 1. Sampling site at the COPAS - UDEC Oceanographic Time Series Station 18, and the nearest SeaWIFS-MODIS satellite recording points used to estimate average primary productivity. Locations of Stations 7 and 26 mentioned in the text are also shown.

ability at the interannual scale and a deepening (50–100 m) of the 40 μM O_2 isoline has been described during El Niño periods associated with coastally-trapped waves and upwelling reduction (Morales *et al.*, 1999).

Sampling and sediment analysis

Surface sediments were collected off Concepción (Station 18, 36°30.8′ S and 73°7.7′ W and ~90 m water depth, Fig. 1) between February and September 2009 with a multiple corer on board the scientific research vessel Kay-Kay II of the Universidad de Concepción. Solid phase phosphorus species in surface sediments (top 0.5 cm) were measured following the sequential extraction method proposed by Ruttenberg (1992) and modified by Schenau and De Lange (2000). In addition, we determined the content of organic and inorganic phosphorus according to Aspila *et al.* (1976). The concentration of phosphorus in all extraction solutions was measured by spectrophotometry at 880 nm (Strickland and Parsons, 1972), except for iron-bound phosphorus, which was estimated by the difference between total inorganic P (Aspila *et al.*, 1976) and the sum of P_{fish}, detrital P and authigenic P. The concentration of oxygen was measured with a CTDO (Seabird SBE-19 equipped with a SBE 42 electrochemical sensor), made available by the Universidad de Concepción COPAS - UDEC Oceanographic Time Series program (www.copas.udec.cl).

Preservation potential

Preservation potential (*Pres%*) of P_{fish} was estimated according to Schenau and De Lange (2000) as

$$Pres\% = 100 \times \frac{P_{fish}dep}{FP \times [P]_{fish} / C}$$

where $P_{fish}dep$ is the deposition rate of the P_{fish} fraction (=0.01 × P_{fish} concentration in mg kg^{-1} × mass accumulation rate in g cm^{-2} yr^{-1}, where 0.01 is a scaling factor used to convert deposition rate units to g m^2 yr^{-1}); *FP* is fish production in the water column estimated with Eq. (1) below, according to Ryther (1969) and Iverson (1990); $[P]_{fish}$ is the phosphorus fraction per dry weight of marine fish (0.03; Anonymous, 1982 cited by Schenau and De Lange, 2000); and *C* is the ratio of fish wet weight to fish dry weight (3.3; Iverson, 1990). Mass accumulation rate is 0.095 g cm^{-2} yr^{-1} (Sánchez *et al.*, 2012).

$$FP = (0.083 \times ACP - 3.08) \times E^n \times 28.5. \quad (1)$$

In Eq. (1), *ACP* is the average phytoplankton annual carbon production (g C m^{-2} yr^{-1}) estimated from four satellite observation points near Station 18 (Fig. 1) available from the SeaWIFS-MODIS database (www.science.oregonstate.edu/ocean.productivity/standard.product.php). *E* is the transfer efficiency of nitrogen assumed to be 0.28 and *n* is the number of trophic levels, assumed to be 2.5 (this value is similar to the one used by Cubillos *et al.*, 1998a, for the coastal upwelling ecosystem off central south Chile dominated by clupeoid fish). The constant 28.5 corresponds to fish biomass C:N (3.6:1) × fish dry weight to C (2.4) × fish wet to dry weight (3.3) (Iverson, 1990). Fish landing data for the BioBio region off central Chile was obtained from the National Fisheries Service (www.sernapesca.cl) and used to interpret fish productivity in the study area.

For statistical analyses, we applied standard linear correlation techniques. However, the data presented in this paper were collected following a temporal sequence and in rigor correspond to a time series. An important assumption for linear correlation analyses is that observations have to be collected independently so that statistical tests are meaningful. If a systematic change over the time interval under investigation is detected within a time series, then the independence assumption is violated and such a trend should be removed. To remove a linear trend we first fitted a least squares trend line to the data, then subtracted the value of the trend line from the original data and obtained a time series of residuals from the trend (i.e., the detrended series; Emery and Thompson, 2006).

Table 1. Minimum and maximum concentrations of oxygen in the water column and width of the suboxic layer ($O_2 \leq 22$ μM) at Station 18 off Concepción during 2009. The symbol "—" represents missing data.

Month	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Nov.
Minimum (μM)	1.0	1.6	5.2	3.7	11.8	2.9	15.1	16.7	5.4
Maximum (μM)	205.7	225.5	282.7	267.8	264.4	247.3	295.5	347.3	343.8
Width (m)	40	50	50	25	—	25	25	—	25

Results

Primary productivity and fish production

Primary production between 2008 and 2009 was the lowest in July (~1 g C m^{-2} d^{-1}) and the highest in December (~8 g C m^{-2} d^{-1}), and followed a seasonal pattern with the highest values registered during the austral spring–summer and the lowest in autumn–winter (Fig. 2a; Supplementary Table S1). Annual primary production varied between 1501 ± 113 g C m^{-2} for 2008 and 1417 ± 136 g C m^{-2} for 2009. The corresponding fish production estimated with the Iverson's (1990) trophic-dynamic model varied between 61 and 143 g C m^{-2} yr^{-1}, depending on the period considered for the primary production estimate (Table 1). Additionally, it is noteworthy that total fish landings lagged primary productivity by four months (Figs. 2a and b; Supplementary Table S2) and was dominated by the common sardine *Strangomera bentincki* with >40% (~7 × 10^5 tons) of the yield disembarked in the BioBio region during 2009.

Oxygen and solid phase phosphorus

Oxygen concentration in the water column at Station 18 ranged from minimal values (2 μM) in February–March to maximal values (>290 μM) in August–November (Table 1). A suboxic layer (<22 μM) was always present below the mixed layer although its thickness varied. This suboxic layer was thicker (40–50 m) and shallower between February and April (austral summer) and thinner (≤25 m) and deeper during the following months (Table 1). Bottom water oxygen varied by one order of magnitude between 2 μM in March and 17 μM in September, and exhibited an increasing linear trend from February to September ($r = 0.75$, $p < 0.05$; Fig. 3a; Supplementary Table S3). Variability in solid phase P species during the study period is shown in Figs. 3b–d. Total sedimentary phosphorus (P_{total}) was on average 1127 ± 126 mg kg^{-1} and was comprised of 60% P_{inorg} (681 ± 50 mg kg^{-1}) and 40% of P_{org} (446 ± 111 mg kg^{-1}). The most abundant inorganic phases were iron-bound P (460 ± 68 mg kg^{-1}) and P_{fish} (221 ± 93 mg kg^{-1}), whereas authigenic and detrital P were below the detection limit (<1 mg kg^{-1}).

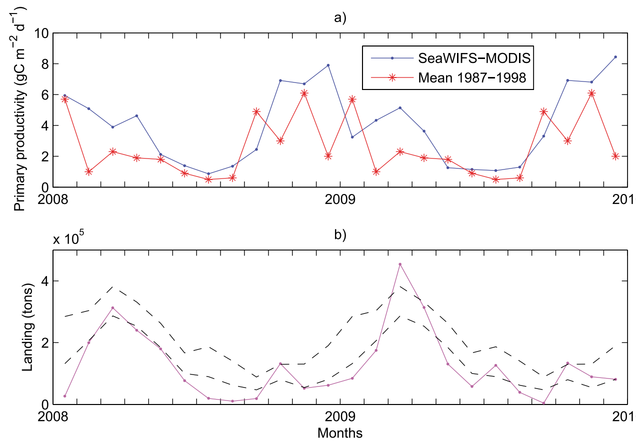

Fig. 2. (a) SeaWIFS-MODIS monthly primary productivity between 2008 and 2009 in the vicinity of the COPAS - UDEC Oceanographic Time Series Station 18, and the monthly average of in situ estimates (O_2 method) by Daneri et al. (2000) at Station 18; (b) fish landing in central Chile between 2008 and 2009 (continuous line) and multiannual 95% confidence intervals (dashed line) estimated for the 1998–2009 interval.

An abrupt decrease in bottom water oxygen was observed in June–July 2009 concurrently with variations in P_{org}, P_{fish} and P–Fe (Fig. 3, Table S3). P_{fish} and P–Fe were negatively correlated ($r = -0.85$, $p < 0.05$, Figs. 3b and d), as was also the case for P_{fish} and bottom water oxygen (Figs. 3a and b). After detrending bottom water oxygen, a negative correlation with P_{fish} was more evident ($r = -0.86$, $p < 0.05$), whereas the correlation between bottom water oxygen and P–Fe despite being relatively high was not significant ($r = 0.56$, $p > 0.05$, Figs. 3a and e). Organic P variability was not statistically related to bottom water oxygenation ($r = -0.22$, $p > 0.05$, Figs. 3a and c).

Preservation of phosphorus from fish remains

Deposition rates of P_{fish} were significantly associated with bottom water oxygen ($r = -0.83$, $p < 0.05$, after detrending bottom water oxygen data) whose variability also coincided with fluctuations of P_{fish} preservation potential between ~7% in June and 30% in July 2009 (Figs. 4a and b; Table S3). Consequently, average preservation

Table 2. *Fish production and P_{fish} preservation potential (Pres%) estimated using SeaWIFS-MODIS primary productivity. Fish production data from 2009 was determined using (i) annual primary productivity during 2008, (ii) primary productivity during spring 2008/summer 2009, and (iii) primary productivity during spring 2008.*

Condition	Primary productivity	Fish production ($g\ C\ m^{-2}\ yr^{-1}$)	Pres (%)
(i) Annual (2008)	1501 ± 113 g C m^{-2} yr^{-1}	143 ± 11	16
(ii) Spring–Summer (2008–2009)	1045 ± 135 g C m^{-2} $semester^{-1}$	98 ± 13	24
(iii) Spring (2008)	660 ± 64 g C m^{-2} $quarter^{-1}$	61 ± 6	38

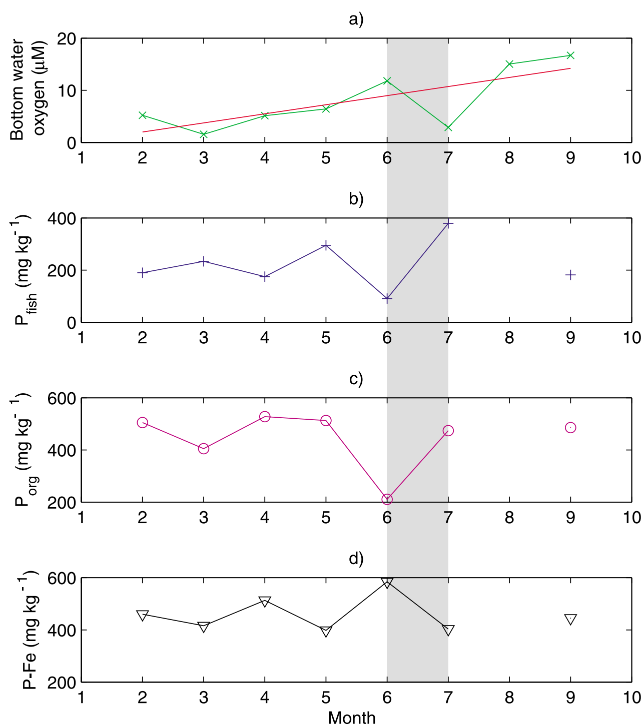

Fig. 3. (a) Average concentration of oxygen at 90 m water depth with a linear trend fitted by least squares superimposed; (b) biogenic P (P_{fish}); (c) iron-bound P (P–Fe); (d) organic P (P_{org}) at Station 18 during 2009. The shaded area corresponds to a period between June and July 2009 with a strong fluctuation of bottom water oxygen.

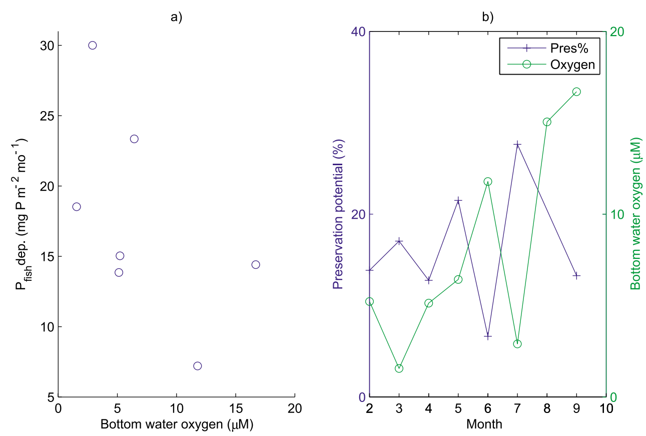

Fig. 4. (a) Biogenic phosphorus deposition rates ($P_{fish}dep$) as a function of bottom water oxygen ($r = -0.83$, $p < 0.05$, after detrending bottom water oxygen); (b) P_{fish} preservation potential (Pres%) derived from total primary productivity during 2008 (1501 ± 113 g C m^{-2} yr^{-1}) and bottom water oxygen at Station 18.

of P_{fish} for the study period was estimated to be $16 \pm 7\%$, following the assumption that off central Chile current fish production is determined by the primary productivity of the previous year (Table 2). Such an assumption seems adequate taking into account the short life span of the common sardine (e.g., Cubillos *et al.*, 1998b, 2002).

Discussion

The results of solid phase phosphorus speciation presented in this paper are, to the best of our knowledge, among the first for the Peru–Chile margin. In a recent study, Holmkvist *et al.* (2010) reported that ~90% of solid phase phosphorus corresponded to P_{inorg} (~40% P_{fish} and >50% P–Fe) whereas the remaining ~10% was made up by P_{org} in the surface sediments of Station 18 during January 2006. These authors did not present P_{fish} absolute contents, which were under their detection limit especially in sediments from the more coastal Station 7 (36°36′ S × 73°0′ W and 34 m water depth, Fig. 1). From the data reported by Holmkvist *et al.* (2010), it is clear that the P_{fish} contribution to total solid phase P at Station 18 was variable with a proportion ≥40% at 1–2 cm and 21–22 core depths, and <5% at core depths between 4 and 5 cm (Holmkvist *et al.*, 2010). In addition, these authors reported an absolute concentration of P_{org} of ~490 mg kg^{-1}, which was similar to the mean value observed by us (~450 mg kg^{-1}), while the P–Fe concentration was >1800 mg kg^{-1}, a value substantially higher compared to ours (~460 mg kg^{-1}). Oxygen at Station 18 fluctuated between 3 and 6 μM in bottom waters (i.e., 90 m water depth) between late December 2005 and the middle of January 2006

(COPAS Oceanographic Time Series). According to the relationship between oxygen concentration and P_{fish} (Fig. 4a), if oxygen levels of ~6 μM at Station 18 persisted until early January 2006, they would have favored P_{fish} preservation and P–Fe dissolution. Such inference is consistent with our results, since P_{fish} and P–Fe were negatively related as expected (Slomp *et al.*, 1996; Slomp and Van Cappellen, 2007). Thus, when bottom waters became relatively more oxygenated, the concentration of oxidized P species increased and P_{fish} content (and preservation) decreased (Figs. 4a and b). A previous report for the study area suggested that fish scale preservation is enhanced with distance from the coast (Díaz-Ochoa *et al.*, 2008). While at Station 18 it was hard to find complete fish scales, a completely different situation was observed ~16 miles offshore at Station 26 (36°26′ S, 73°23′ W and 120 m water depth), where the upper ~10 cm of the sediment column were characterized by the presence of abundant jack mackerel fish scales, bones and vertebrae (Díaz-Ochoa *et al.*, 2008). This pattern appears to be confirmed by the higher proportion of solid phase P_{fish} at Station 18 compared to a site closer to the coast (Station 7; Holmkvist *et al.*, 2010).

Our results showed that several solid phase inorganic P species were sensitive to changes in bottom water and sediment oxygenation (Figs. 3 and 4). We also expected organic P to be released under both oxic and anoxic conditions, however no clear pattern was observed under the shifting oxygen levels in bottom waters during the study period (Fig. 3c). Based on average value of P_{org} and assuming an organic carbon content of 2% in surface sediments at Station 18 (Muñoz *et al.*, 2012), we estimated a sedimentary molar ratio $(C/P)_{org} \approx 117$, which was very close to the Redfield ratio. This indicates that sedimentation rates (0.27 cm yr^{-1}; Muñoz *et al.*, 2012) in the study area appear to overwhelm the rate of P_{org} degradation in recently deposited sediments and that short-term oxygen fluctuations do not apparently affect P_{org} preservation. Similar behavior has been reported for other low oxygen sedimentary settings, such as the Saanich Inlet (see figure 3 in Slomp and Van Cappellen, 2007).

The preservation potential based on estimated fish production for 2009 showed increased deposition of P_{fish} during the year, but this rate was negatively affected as bottom water oxygen concentrations increased (Fig. 4b). This was especially true during June and September when oxygen concentrations increased above 8.3 μM and P_{fish} decreased below 200 mg kg^{-1} (Figs. 3a and b). Furthermore, P_{fish} and P–Fe varied inversely suggesting that when oxygen in bottom waters increased, part of the orthophosphate released from fish debris ended up being adsorbed onto iron oxides. In the study area, it has been shown that during summer, when suboxia develops, orthophosphate is released from the sediments to the water column, whereas during autumn and winter, when the system is slightly oxygenated and iron sulfides are reoxidized, phosphate, which is linked to trivalent iron, tends to precipitate (Holmkvist *et al.*, 2010). Thus, we observed that biogenic apatite was well preserved in surface sediments in coincidence with Holmkvist *et al.* (2010) who found that biogenic phosphorus accounted for ~40% of solid phase P species at depths between 1 and 2 cm in two sediment cores collected at Station 18. However, at greater depths, very low concentrations of biogenic P (P_{fish}) were reported by these authors at core depths between 2 and 10 cm and higher concentrations below this depth, where substantially higher contents of biogenic apatite were observed (Holmkvist *et al.*, 2010). This fact could be interpreted as the occurrence of a less favorable environment for P_{fish} preservation during the last decades in the study area. Therefore, our results support the view that iron oxides in the sediments of Station 18 act as a reservoir of reactive phosphorus released both from organic matter and the dissolution of fish remains, especially during fall and winter. During summer, we detected insignificant authigenic apatite formation as shown before by Holmkvist *et al.* (2010), which is contrary to what we would expect since sediments and bottom waters during autumn–winter are saturated with phosphate, and carbonate is not a limiting factor (Holmkvist *et al.*, 2010). Future research is needed in order to elucidate whether authigenic apatite precipitation is limited by fluoride availability and/or the transient (seasonal) nature of the OMZ in this area that would prevent authigenic apatite accumulation at Station 18 if oxygenated waters prevail (Holmkvist *et al.*, 2010).

Solid phase phosphorus and oxygen minimum zone fluctuations

The upwelling area off Concepción is characterized by the seasonal development of an oxygen minimum zone during spring-summer and its subsequent destruction during fall (e.g., Paulmier *et al.*, 2006 and references within). Throughout the studied period, however, and despite the thickening of the suboxic layer in summer and its thinning during fall and winter, suboxic conditions below the mixed layer did not disappear completely. Variations in the strength of the OMZ are probably important to determine solid phase P dynamics in the study area. This conclusion is in agreement with observations made by Takesue *et al.* (2004) who found that the ratio Cd/P in upwelled waters during spring-early summer in Coliumo Bay (central Chile) was lower than expected (0.27×10^{-3} mmol mol^{-1}) compared to the California upwelling system (0.35×10^{-3} mmol mol^{-1}). These authors suggested that the proportion of Cd:P in upwelling waters could be altered when surface sediments are anoxic since Cd precipitates into pore waters as a sulfide and P is released from sediments. Such an input of phosphate into bottom waters could add to the fertilization effect of upwelling. Our data suggests that solid phase phosphorus speciation in the coastal sea off Concepción (Station 18) is sensitive to strength of the OMZ (Fig. 3).

The very high primary production typical of central south Chile also sustains high fish production, evidenced by yields of $>1.6 \times 10^6$ tons during 2009. More than sixty percent of this production is made up by the common sardine (*Strangomera bentincki*) and anchovy (*Engraulis ringens*), two short-lived species that constitute a fishery largely sustained by catches of juvenile fish (ages ~6 months; Cubillos *et al.*, 1998b, 2002; Arteaga and Cubillos, 2008). As a consequence, the small pelagic fishery in the study area is strongly seasonal and the fishing effort is concentrated during the upwelling season when cohorts spawned around July of the previous year are recruited. The dynamics of the fishery described so far may explain the lag between biological productivity and the maximum fish yield (Fig. 2a). In addition, due to the life cycle characteristics of the dominant clupeoid fish in the ecosystem over the shelf off Concepción, most fish remains that reach the upper sediment layer likely correspond to common sardines and anchovies. Thus, our estimate of P_{fish} preservation potential during 2009 derived from primary production during 2008 appears to be reasonable. Moreover, since the abundance of species, such as common sardine, is in part determined by spring primary production (Gómez *et al.*, 2012), a P_{fish} preservation potential of 16% can be considered a fairly conservative value (Table 2).

This study was focused on surface sediments, and therefore has mainly described temporal changes in P_{fish} preservation potential as a function of bottom water oxygenation over an annual cycle. However, little is currently known about the behavior of solid phase P species within the study area. The only previous report available is the work conducted by Holmkvist *et al.* (2010) who found that P_{fish} was mostly absent from the upper 21 cm at Station 18 (i.e., the last ~80 years). Since this work covered a quasi-annual range (summer through late winter) we could show that a substantial fraction of P_{fish} was effectively accumulated and preserved within the sediments under a range of bottom water oxygen concentrations typical of suboxic waters (1.6–16.7 μM). This finding suggests that P_{fish} is useful as a proxy for fish abundance in the study area even though injection of oxygen is verified in surface waters during the winter season, apparently not affecting P_{fish} preservation. Based on our results we suggest that suboxic sediments underneath seasonal oxygen minimum zones such as that found off Concepción are suitable to carry out studies addressed to infer fish abundance fluctuations in the past. So far this study is the first directly addressing the study of P_{fish} (biogenic P) preservation in this upwelling ecosystem and more research is necessary to establish whether the upwelling system is currently experiencing changes that favor the preservation of fish remains, and whether these changes are related to variation in primary production and/or the amplitude of seasonal oscillations of the oxygen minimum zone.

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Supplementary Materials

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Tables S1 to S3