The effect of bioturbation on the retention of phosphorus in Iberian continental sediments (offshore Porto)

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1. Introduction

A considerable proportion of pelagic primary production reaches the seafloor in the continental margins (Jorgensen, 1983). As organic matter is mineralised in the sediment, dissolved PO_4 is released to the porewater, retained in the sediment solids and diffused to the overlying water, where it can be available again for uptake by phytoplankton (Howarth *et al.*, 1995). This cycle is accelerated in areas of coastal upwelling as the NW Iberian Margin (Wooster *et al.*, 1986; Fiúza *et al.*, 1982; Silva, 1992).

Phosphorus retention and release in marine sediments are usually considered to be redox-dependent. If the oxidised surface sediment layer is thin or absence the PO₄ released from organic matter can escape to the overlying water. When oxidised layer grows, substantial amounts of PO₄ can be retained through the adsorption to Fe oxides. This adsorption process allows only limited diffusive transport of PO₄ to the overlying water, and buffers the PO₄ concentrations (Krom and Berner, 1981; Sundby *et al*, 1992; Jensen *et al*, 1995). In spite of that the oxidised layer may not prevent the release of dissolve PO₄ from sediments (Slomp *et al*, 1998): when organic matter deposited on the sediment is rapidly mineralised (Martens *et al*, 1978); transport of pore water caused irrigation (Boudreau, 1984; Aller and Yingst, 1985); the adsorption to Fe oxides is partially reversible (Sundby *et al*, 1992).

This work reports the concentration of PO_4 in pore water and in solid sediments from the NW Iberian continental margin and the effect of bioturbation and irrigation on the incorporation of P to Fe oxides.

2. Study Area

The study was carried out in a muddy patch located 15-25 km Northwest off Douro River in the NW Iberian Margin (Fig. 1). This deposit is located between 65 m and 130-m depth, and is 42-km long (N-S) and 18-km wide. The formation is limited on the west side by Cretaceous and Palaeocene outcrops (mudstones and detritic mudstones, respectively) and is 5-30 m high (Drago *et al.*, 1994). The deposit is characterised by a silt-clay fraction (Dias and Nittrouer, 1984; Magalhães, 1993), and its age was estimated at 2000 yr BP (Drago, 1995). The area is still an active deposit of particles transported from the continent. The general circulation over the northern Portuguese continental shelf is mainly forced by the wind regime: northerly summer winds favours coastal upwelling (Wooster *et al.*, 1976; Fiúza *et al.*, 1982) and W-SW winds in winter are responsible for downwelling conditions (Vitorino, 1989).

3. Sampling and Methodology

Sediment cores of 30-cm length were collected at the Douro muddy complex in January 1998 and in May 1998 (Fig. 1). The sampling was performed with a multi-corer on board the research vessel Mestre Costeiro. The cores were described and sliced on board, and the samples kept in a refrigerated chamber. The co-ordinates of the sampling stations of the two missions are presented in Table I. The lithological composition of the sediment samples was determined in the core A1, B1, C1 and E1 with a MALVERN 3600E laser diffraction for determination of particle size in Department of Oceanography and Geology of Bordeaux University. The carbonate content of the same cores was measured by the volumetric method described in Vatan (1967). The ²¹⁰Pb radiochronology was performed at several layers of the cores at the cited department (Clifton and Hamilton, 1979).

Core	Sampling	Coordinates	Water	Length
	date		depth (m)	(cm)
A1	January	41°10.041'N 9°02.379'W	93	28
B1	January	41°12.200'N 9°02.299'W	94	30
C1	January	41°14.310'N 9°02.001'W	95	24
E1	January	41°19.300'N 9°00.002'W	88	28
B2	May	41°12.200'N 9°02.299'W	94	28
G2	May	41°14.450'N 8°58.000'W	72	28

Table 1 - Coordinates of the sampling stations



Figure 1 - Map of the Douro muddy complex and the position of the sampling stations

For the remaining analysis the sediment samples were centrifuged for 30 min. at 3,000 r.p.m. and 4°C to separate the pore water from the solid phase. Supernatant water was filtered through 0.45 μ m Millipore filters and analysed the content on total dissolved Fe, total dissolved Mn and dissolved PO₄³⁻. Dissolved Fe and Mn were determined by flame atomic absorption, and phosphate by molecular absorption (Grasshoff, 1976). Levels of total Fe and Mn, acid volatile sulphide (AVS), amorphous iron hydroxides (FeOOH) and phosphate were determined in the solid phase. AVS was measured according to Henneke *et al.*, (1991) and Madureira *et al.* (1997). Sulphides from AVS were released with 1 M HCl and determined by voltammetric methods using a Metrhom apparatus equipped with a 693 VA processor and a 694 VA stand. Phosphate simultaneously extracted with AVS were determined by molecular absorption (Grasshoff, 1976). The amorphous iron hydroxides and the associated phosphate were obtained from an ascorbate extraction according to method described in (Anschutz *et al*, 1998). Iron hydroxides were analysed by flame A.A. and the phosphate by UV spectrophotometry.

4. Results

4.1. Core description

The cores collected during the two missions were characterised by homogeneous moderate olive brown (5y 4/4) and olive grey (5y 3/2) silty-clayed mud. In general, sediments sampled in January 1998 (A1, B1 and C1) contained gastropod and bivalve shells, with the exception of core E1 where no organisms were detected. The cores collected in May 1998 (B2, G2) exhibited higher density of shells, living worms and several hollow tubes.

4.2. Grain-size distribution, water and carbonate content

The mean grain-size was relatively uniform in the analysed cores, but it was notorious an increase towards the surface from 20 μ m to around 40 μ m. The vertical profile of the core B1 presented in Figure 2 is illustrative of the pattern observed in the area. This increase means that recently deposited material is coarser, which may indicate a strong hydrodynamic episode. Water content varied with the grain size and ranged from 40 to 55%. Carbonate content of the sediments was relatively uniform, ranging between 3 and 6%. In general, vertical distribution of carbonate content is related to the sand percentage (Fig. 3).



Figure 2 - Mean grain-size (μm) of the core B1



Figure 3 - Vertical profiles of sand (%) and carbonate contents (%, thinner line) of the core E1

4.3. Sedimentation rate

For all the analysed cores (A1, B1, C1 and E1) the activity begins approximately at 10 dpm g⁻¹ and ends to a value close to zero around 20-cm depth. A representative profile of the ²¹⁰Pb excess vertical distribution in the studied area is shown in Figure 4. In addition, the ²¹⁰Pb activity profiles were relatively constant in the first 10 cm, which may be attributed to the reworking of upper sediments presumably due to bioturbation. On the basis of the ²¹⁰Pb excess values, (excluding the bioturbated upper layers), the maximum sedimentation rates have been estimated between 0.30 cm yr⁻¹ and 0.44 cm yr⁻¹. The first 18-20 cm sediment layers were, then, deposited between 40-60 yr ago.

4.4. Phosphate, iron and manganese concentration in sediment pore water

The vertical profiles of $PO_4^{3^2}$, total dissolved Fe and total dissolved Mn of the cores E1, G2 and B2 are represented in Figure 5. Two contrasting patterns were found. Profiles of core E1 are relatively well defined with a concentration enhancement in the upper sediment layers. Otherwise, profiles of the cores G2 and B2 were irregular with successive maximum and minima.

In addition, concentrations increase below 8-cm depth, which contrasts with the higher values, found in the upper layers of the core E1. Levels of the three parameters were comparable in cores E1 and G2 and lower in B2 that may be related to specificity of this site. The two types of vertical profiles indicate that production Mn, Fe and PO_4^{3-} in core E1 is close to sediment surface, as predicted by the thermodynamic sequence of the oxidation reactions of organic matter (Froelich *et al*, 1979).



Fig. 4 – The 210 Pb excess activity profile in the core A1



 $\label{eq:Figure 5-Vertical profiles of phosphate, total dissolved Fe and Mn~(\mu M) \\ in pore waters from the cores E1, B2 and G2.$

The absence of chemical zonation in the other two cores and the increases of Mn, Fe and $PO_4^{3^-}$ in lower sediment layers are on line with the presence of bioturbation of these samples. The activity of the benthic macrofauna is normally responsible for changes of vertical profiles (Hines, 1991). Because results were obtained only in two periods they do not elucidate whether the organisms are seasonally present or more abundant in certain areas of the muddy patch. However, B1 and B2 collected at the some site in January and May, respectively, contained polychaets only in spring, which may indicates a seasonal distribution of these organisms.

4.5. Iron oxides and acid volatile sulphide (AVS) in the solid phase

The iron profiles obtained from the ascorbate extraction (mainly amorphous iron hydroxides) and the AVS (mainly iron monosulphides) in the cores E1, G2 and B2 are presented in Figure 6. Iron oxides and acid volatile sulphide (AVS) profiles of the non-bioturbated core (E1) showed opposite trends: amorphous iron hydroxides decreased in the first 4-cm remaining relatively constant, and sulphide production began below the 4.5-cm depth. The distributions indicate an oxic/suboxic layer of approximately 4.5 cm and anoxic sediments below that depth. This pattern is predicted by the thermodynamic sequence of organic matter oxidation reactions. In contrast with this situation, the iron concentrations determined in the bioturbated cores G2 and B2 increased in the deeper layers of the sediment, and AVS showed irregular profiles with successive maxima and minima below the first 4.5-cm. The results show absence of chemical zonation in these cores, and indicate the presence and activity of the benthic macrofauna affect deeper sediment layers than 8 cm.

Figure 6 –Vertical profiles of Fe extracted with ascorbate method and AVS (µmol g⁻¹) in the cores E1, G2 and B2.

4.6. Phosphorus associated with iron oxides

The comparison of phosphorus and iron concentrations and of Fe/P ratios in the cores E1, G2 and B2 is presented in Figure 7. As mentioned previously (Fig. 5) iron oxide profiles are different in the two sets of cores (E1 and G2, B2). Amorphous iron oxides increase towards deeper sediments of the

bioturbated cores and phosphorus concentrations of the cores G2 and B2 exceeded the levels found in the non-bioturbated core (E1). Furthermore, phosphorus concentrations exhibited increase and decreases in successive sediment layers. This irregularity was not observed for iron, presumably due to high quantity present, but such a pattern was clearly discerned AVS that has lower levels (Fig. 6). The Fe/P ratio presented different values at the three cores and was not constant with the depth. Higher ratios were found in core E1, which presented lower P concentrations.

Figure 7 – Vertical profiles of Fe oxides, associated P and Fe/P ratio in the cores E1, G2 and B2.

4.7. Relationships between phosphorus and iron oxides and AVS

The relationships between P and Fe oxides and between P and AVS are shown in Figure 8. In both cases the points corresponding to the core B2 are plotted in a different area of those from the core E1. The amount of P associated with amorphous iron oxides (P-oxides) was higher in B2 (irrigated core), while the quantity of P simultaneously extracted with metal sulphides (P-AVS) was much lower than that present in E1. This contrast distribution indicates that bioturbation causes an additional incorporation of P in solids, namely Fe oxides. A constant Fe/P ratio as observed by Anschutz *et al* (1998) was not found in this work.

Figure 8 – Relationships between P and Fe oxides and P-AVS (simultaneously extracted) and AVS in the cores E1 and B2

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