VERTICAL PROFILES OF P, Fe, Mn, AVS AND TRACE ELEMENTS IN SEDIMENT CORES OFF PORTO

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Introduction – Objectives

Sediment is a very important compartment for the phosphorus cycling in the marine environment. Phosphorus is transported to the sediment by the biogenic particles, phosphate is regenerated to pore water during the oxidation of organic matter and eventually phosphate interacts with the iron cycling due to its affinity to iron oxides (Anschutz et al, in press). On the other hand Fe is strongly involved with Mn and S, which means that P cycling in the sediment may be rather complex. The objective of the report is to evaluate the importance of these interactions in the coastal area off Douro estuary

Methodology

The studies were carried out in the muddy patch located north-west off Douro river. This muddy complex is located 15-25 Km from the coast, at depths between 65 and 130 meters, with 42 Km length (N-S) and 18 Km width and its silt-clay fraction frequently exceed 90 % (Drago et al., in press) (Figure 1).

Near-bottom water were collected in several areas of the muddy complex during the cruise of the R.V. "Almeida Carvalho" in December of 1997. The co-ordinates of the stations are presented in Table I. In addition, water samples were collected at different depths of the water column in station 49. Dissolved phosphate was determined using an autoanalyser SKALAR equipped with a 6250 photometer and a 2532 autosampler.

Stations	Latitude	Longitude
19	41° 08.8' N	9° 11.6' W
20	41° 08.9' N	9° 05.6' W
29	41° 13.9' N	8° 57.6' W
31	41° 14.0' N	9° 06.9' W
33	41° 13.9' N	9° 13.7' W
48	41° 20.1' N	9° 06.0' W
49	41° 20.2' N	9° 02.1' W
50	41° 20.2' N	8° 58.2' W
57	41° 25.0' N	9° 00.6' W
58	41° 25.0' N	9° 00.6' W

Table I - Co-ordinates of the water stations

Sediment cores of 30 cm length were sampled in the Douro muddy complex during the cruise of the research vessel "Mestre Costeiro" in January of 1998. The sediment was collected with a Multicorer in station 59 (41° 19.3'N; 9° 00.0'W). From the several replicates obtained, one sediment core was sliced in layers of 0.5 cm in the first 5 cm depth, in layers of 1 cm till 10 cm and in 2 cm to the 30



Figure 1 - Vertical profile of phosphate (μ M) in the water column in station 49.



Figure 2 - Phosphate concentrations (µM) in near-bottom water.

cm. The sediment samples were stored in Oak ridge leakproof polycarbonate tubes, completely filled up and 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 phosphate. Fe and Mn were determined by flame atomic absorption and phosphate according to the method referred above.

In the solid phase it was determined total Fe, Mn, Cu, Pb and Cd; acid volatile sulphide (AVS) and simultaneously exctrated metals (SEM), 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. The simultaneously extracted iron (Fe_{SEM}) was analysed by flame A.A. The simultaneously extracted trace elements (Cu, Pb and Cd) were analysed by atomic absorption using an UNICAM 939 equipped with an UNICAM GF 90 furnace. The amorphous iron hydroxides and the associated phosphate were obtained from an ascorbate extraction according to method described in Anschutz et al (in press). Fe and Mn were analysed by flame A.A., Cd, Cu and Pb with the furnace and the phosphate by UV spectrophotometry.

Results and discussion

Vertical Profiles of Phosphate. The vertical profile of phosphate concentrations in the water column of the station 49 in shown in Figure 1. Phosphate concentration increased sharply near the bottom, suggesting a phosphate regeneration near the sediment-water interface. The levels of phosphate concentrations near the bottom in all the studied stations are presented in Figure 2. The levels vary from station to station (between 0.18 and 0.86 μ M) which may be interpreted as different regeneration intensities. The vertical profile of phosphate concentration in the pore water from the 30-cm core is presented in Figure 3.



Figure 3 – Phosphate concentrations in the pore water sediments along the 30 cm depth

Phosphate increased up to $83 \ \mu\text{M}$ below the sediment-water interface. This profile points out to a sediment layer of phosphate regeneration centred at 5 cm depth. The pore water values were two orders f magnitude higher than the levels measured in the water column (fig. 4).



Figure 4 - Vertical profiles of phosphate concentrations (μ M) obtained in the water column and in the sediment pore water

Predicted flux of phosphate from the sediment. Using the first Fick's law we can calculate the molecular diffusion flux of phosphate from the pore water to the water column. This predicted flux is described by the equation:

$$J_i = -\phi^3 Ds (\Delta C / \Delta x)$$

Where $Ds = 5x \ 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $\phi = 0.3$, ΔC is the phosphate variation across the interface and Δx is the corresponding distance. Assuming $\Delta C = (83-3) \ \mu M$ and $\Delta x = (4.5 - 0) \ \text{cm}$, we obtain a flux of phosphate out of sediment of 2.07 $\mu \text{mol m}^{-2} \text{ d}^{-1}$. Presumably this amount accounts for the increase of phosphate concentrations in the near-bottom water.

Comparison of P, Fe, Mn and AVS profiles in the upper sediments. The vertical profiles of phosphate, iron and manganese concentrations in the pore water are shown in Figure 5. Iron and manganese concentrations varied from 0.7 to 83.3 μ M and from 2.3 to 8.9 μ M, respectively, and the highest values were obtained just below the surface. The figure illustrates also that the peak of phosphate production appeared below the layers of higher iron and manganese production.



Figure 5 – Concentrations of phosphate, P (μ M), iron, Fe (μ M) and manganese, Mn (μ M) in the sediment pore water

Concentrations of amorphous iron hydroxides in the solid phase obtained by the ascorbate extraction varied from 0.066 to 0.104 % and the levels decreased in the first 5 cm remaining relatively constant thereafter (fig. 6). Comparing these results with the phosphate concentrations obtained in the pore water (fig. 3) we can observe that iron in solids decreased with the depth in the upper sediment layer, while phosphate in pore water increases in the sub-oxic layer. Thus, the low concentrations of phosphate in pore water occurred in the layers enriched in iron oxides.

A comparison of amorphous iron hydroxides profile with the AVS concentrations is presented in Figure 6. AVS concentrations varied from 0.3 to 17.8 μ mol g⁻¹, d.w. and displayed a clear-cut increase below 4.5 cm, varying then within shorter intervals.



Figure 6 – Concentrations of amorphous iron hydroxides, FeOOH (%) and acid volatile sulphide, AVS (μ mol g⁻¹, d.w.) obtained in the solid phase of the sediment.

The iron hydroxides and the AVS profiles showed an opposite trend. Iron hydroxides decreased in the first 4 cm and sulphide production begins below the 4.5 cm indicating an anoxic sediment below this depth.

The iron profiles obtained from the ascorbate extraction (mainly amorphous iron hydroxides) and the iron concentrations resulting from the AVS extraction (Fe_{SEM}) are presented in Figure 7. These two profiles showed opposite trends. Simultaneously extracted iron (Fe_{SEM}) increases with depth, presumably reflecting the formation of amorphous iron sulphides. Sulphide precipitation starts between the 0.5 and 1.5 cm depth and proceed until the 3.5 cm. Below this depth remain relatively constant with a small increase after 15 cm. This vertical distribution is quite different from that obtained with the ascorbate extraction, which seems to show the amorphous oxides.



Figure 7 – Comparison of iron concentrations in the solid phase obtained by the ascorbate extraction, FeOOH (%) and by the AVS extraction, Fe_{SEM} (%).

Phosphate concentrations in the solid phase obtained from the ascorbate extraction varied from 0.31 to 0.49 μ mol g⁻¹ and the profile is shown in figure 8. Phosphate concentrations were relatively constant in the first 10 cm showing a certain irregularity below this depth. The molar ratio Fe/P is also presented in figure 8. The ratio varied, in general, from 30 to 50 and the higher value was obtained near the surface. In the oxic/sub-oxic layer the ratio Fe/P is not constant and decrease as iron hydroxides concentration decreases.

Vertical distribution of trace elements in the solids. In figure 9 are represented the vertical profiles of Cd, Cu and Pb from the AVS extraction (Cd_{SEM}, Cu_{SEM} and Pb_{SEM}). As observed for Fe_{SEM} these trace elements also show an increase in SEM concentrations at 1.25 cm depth. Cu_{SEM} shows a maximum a 1.75 cm and Cd_{SEM} and Pb_{SEM} present double peaks at same depth and below (4.5 cm).



Figure 8 – Vertical profiles of phosphate concentrations, P (μ mol g⁻¹) and the molar ratio Fe/P obtained in the solid phase of the sediment.



Figure 9 – Vertical profiles of simultaneously extracted cadmium, Cd_{SEM} (µg g⁻¹), copper, Cu_{SEM} (µg g⁻¹) and lead, Pb_{SEM} (µg g⁻¹) in the solid phase.

Total trace metals (Cd, Cu, Pb) concentrations corrected to aluminium variations did not show remarkable differences (fig. 10).



Figure 10 – Total concentrations of cadmium, copper and lead corrected to aluminium content in the solid phase of the sediment (Cd/Al, Cu/Al, Pb/Al).

References

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