



Phosphorus speciation in sediments and assessment of nutrient exchange at the water-sediment interface in a Mediterranean lagoon: Implications for management and restoration



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ABSTRACT

Bioavailable P-forms in Bizerte lagoon and the adjacent open waters of the north-eastern Mediterranean, were quantified with the SEDEX sequential extraction method. Pore water analysis, sediment total organic carbon and the mineralogical composition of sediment samples were also determined and potential P release at the lagoon's water-sediment interface was assessed through benthic chamber experiments. Sediment shows an abundance of quartz and calcite in different core samples from the lagoon center, while pyrite is observed in samples from the open sea. Relative abundance of Fe-bound phosphorus in the sediments reveals the co-precipitation of both constituents as P-containing iron (oxyhydr) oxides. Phosphorus bioavailability was greater in the lagoon than in the open sea, dependent on Ca–P fractionation, and promoting P sediment immobilization. Pyrite presence is related to periodic anoxic events inducing P release upwards in relation to periodic increases in organic loads.

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1. Introduction

The surface layer of the eastern Mediterranean is mainly comprised of the Atlantic waters arriving from the Atlantic Ocean through the Strait of Gibraltar. The usual nutrient-poor Atlantic Tunisian Current (Ben Ismail et al., 2012, 2014), originating in the Tunisia-Sicily channel, flows along the Tunisian coast to reach different zones, including Bizerte lagoon where increased eutrophication in its water quality is detected (Ben Ameer et al., 2013). Indeed, studies conducted over the years, describing phytoplankton dynamics in relation with nutrient availability in the lagoon water column, have demonstrated the role of anthropogenic nutrients in triggering harmful algal blooms (Sahraoui et al., 2009; Smida et al., 2012; Turki et al., 2014), with the ability of some strains to cause shellfish poisoning (Turki et al., 2014) and/or to form resting cysts which accumulate in the sediments (Fertouna-Bellakhal et al., 2014). Information on the status of phosphorus in

the sediment, on the other hand, is totally lacking. Yet when trapped in sediment, this element may, under precise conditions (Alaoui et al., 1994, 2014; Andrieux-Loyer et al., 2008), be released upwards as a biologically available nutrient that will support phytoplankton growth (Aleya, 1992). Since summer in the lagoon is characterised by low watershed input, with the N/P in the water column higher than the Redfield ratio (16), thus suggesting phosphorus limitation, we hypothesised that phytoplankton growth during the summer hypolimnetic anoxia might be supported by the diffusive fluxes from the water-sediment interface. It was therefore urgent to investigate phosphorus speciation so as to understand the association of sediment bound to P, and to undertake benthic chamber experiments in order to estimate the potential release of phosphorus and thus help to propose management tools to mitigate the lagoon's eutrophication.

In the Mediterranean, many studies have been carried out to investigate fractionation and sorption/desorption of P in surface sediment (Krom et al., 2003, 2010), with the sequential chemical extraction of P selected as the most suitable means to examine these processes (Eijssink et al., 1997; Anderson and Delaney, 2000).

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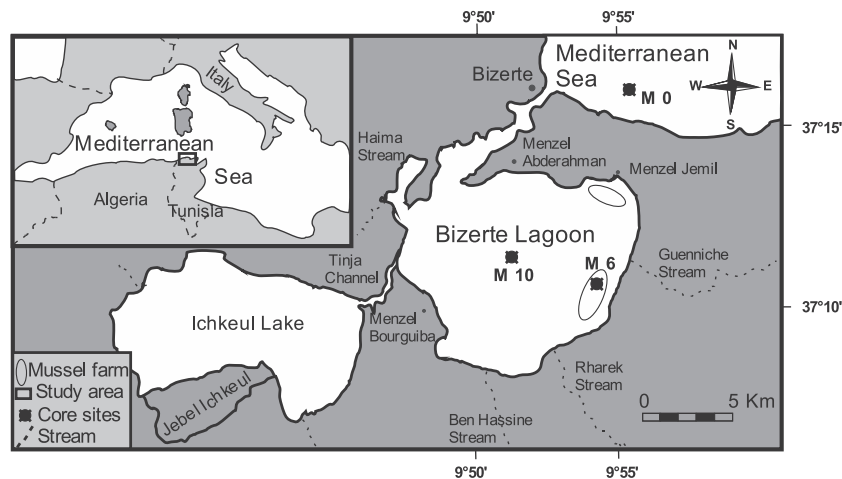


Fig. 1. Geographical position of the studied area in Tunisia and localization of the investigated core sediment in the Mediterranean Sea and Bizerte lagoon.

Phosphorus can be associated with Fe, Ca oxides and Al or be adsorbed on the surface of minerals and organic materials, with salinity, pH or redox potential regulating the relative importance of each fraction (Avilés et al., 2006; Van der Heide et al., 2010). However, no such information is available for the north-eastern Mediterranean.

This study aims to (a) improve our understanding of P fractionation in core sediment samples, (b) determine the proportion of available phosphorus fractions and (c) evaluate their possible contributions to P release in Bizerte lagoon, especially during periods of hypolimnetic anoxia.

2. Materials and methods

2.1. Study site

Bizerte lagoon in northern Tunisia is connected to the Mediterranean Sea from its eastern shore by a narrow (300 m wide) channel. Connected to Ichkeul Lake from its western shore by a channel approximately 5 km long (Fig. 1), the lagoon has a surface area of 121.6 km² and maximum and mean depths of 12 and 8 m. Salinity in the lagoon ranges from 33 to 35 p.s.u., whereas in the inlet it is similar to that of sea (36 p.s.u.). The total amount of fresh water discharged into the lagoon is 125 Mm³ y⁻¹. The lagoon's environment is threatened by anthropic interferences, yet a large mussel farm operates there, mainly in the eastern zone (Fig. 1). In addition to marine and continental influences, the lagoon is affected by urban and industrial effluents. The southern part of the lagoon contains an iron factory and a shipyard, but the northern part, receiving abundant industrial waste, is the part most affected by human activities.

2.2. Sampling and processing

Three core samples were manually retrieved from the bottom of the lagoon by scuba divers: an open sea core at 22 m depth opposite the city of Bizerte (Core M0: marine station) and two cores inside the lagoon (Cores M6 and M10, at 8 m and 12 m depth, respectively) (Fig. 1). Samples were collected by inserting 60 cm long polyethylene tubes with a 9 cm diameter into the sediment. The collected core sediments were opened immediately under strict anoxic conditions in a nitrogen-filled glove box to prevent oxidation. The subsamples were transferred under N₂ atmosphere into centrifugation tubes for pore-water extraction through centrifuging for 30 min at 3000 rpm. The supernatant pore water was filtered, under an N₂ atmosphere, using a Minisart[®] NML

syringe filter with 0.45 μm pore size, then placed in clean sample bottles and frozen at -20 °C. Sediment subsamples were then also stored at -20 °C.

2.2.1. X-ray diffractometer (XRD) analysis and scanning electron microscopy (SEM) observation

Mineralogical analyses were carried out by means of a PANalytical X'Pert PRO (XRD). The different mineral phases were evaluated with the X'pert HighScoreplus[®] programme. Pyrite was observed by means of an ESEM Type JEOL JSM -5400 scanning microscope.

2.2.2. Phosphorus fractionation

To understand the cycling of P in the Mediterranean and its effect on present times, greater insight into this element's behavior in western Mediterranean sediments is crucial. Ruttenberg (1992) published a sequential extraction technique for marine sedimentary phosphorus (the SEDEX method) which, according to Eijssink et al. (1997), applies to Mediterranean sediments. In order to estimate the amount of bioavailable P, five major forms of solid-phase P in sediments were determined using the SEDEX procedure (Ruttenberg, 1992; Akhurst et al., 2004):

- 1) Exchangeable or loosely bound labile P (lab-P) using MgCl₂ as an extractant,
- 2) Ferric-bound (oxide associated) P (Fe-P) using citrate-dithionite-bicarbonate (CDB) solution,
- 3) Calcium carbonate associated P, authigenic carbonate fluorapatite and biogenic apatite (Ca-P) extracted with 1 M sodium acetate buffered to pH of 4.0 using acetic acid,
- 4) Detrital apatite P of igneous or metamorphic origin (detr-P) using HCl dissolution at a low pH and
- 5) Organic P (org-P) using dry oxidation at 550 °C and residue dissolution with HCl dissolution at a low pH.

Steps 2 and 3 are comprised of sub-steps consisting of MgCl and water washes, which prevent dissolved P from readsorption on sediment surfaces. In addition, in step 3, due to high CaCO₃ contents recorded in Mediterranean sediments (more than 60%, this percentage being higher than in other areas such as the North Atlantic), we allowed for additional shaking time as proposed by Eijssink et al. (1997). Phosphorus was analyzed by spectrophotometry using the standard phosphomolybdate blue method (Koroleff, 1976) which cannot, however, be used directly for the CDB solutions since its extractant interferes with the molybdate blue reagent. These solutions were first reacted with a 1% v/v FeCl

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