Oxygen consumption and nutrient fluxes in coastal marine sediments off the Mejerda River delta (Gulf of Tunis)

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Research Article

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Abstract

The authors studied the benthic flux of oxygen, dissolved iron and manganese, and nutrients *in-situ* at three points in the Mejerda River Delta, at depths of 10 m, 20 m, and 40 m, in March and August 2012. Three sedimentary cores were simultaneously drilled, at the same locations, to determine the diffusive flux of Fe^{2+}, Mn^{2+}, NO_3^-, NH_4^+, and PO_4^{3-} and to estimate the diagenetic mechanisms occurring below the sediment–water interface. Photosynthesis was not sufficiently high during the day and the oxygen consumption at the sediment-water interface was about 1.7 to 10 mmol/m²/day, essentially controlled by the degradation of organic matter and oxidation of reduced elements. Nitrate contents were relatively high in the sediment (above 140 μM for NO_3^-) and their production was not always in conformity with the general scheme of early diagenesis, moreover, the benthic flux between the water and sediment was not clearly established. The diffusive flux of NH_4^+ and PO_4^{3-} was always directed to the water column, at averages of 1.27 μmol/m²/day for PO_4^{3-} and 96.5 μmol/m²/day for NH_4^+, complying with those measured by the benthic chambers, but representing less than 30% of the benthic fluxes for NH_4^+ and less than 5% for PO_4^{3-}.

Keywords: Early digenesis, nutrients, oxygen, benthic flux, diffusive flux, sediment-water exchanges.

Introduction

The nutrients (nitrites, nitrates, phosphates, and ammonium) and oxygen are important elements of biogeochemical cycles, and their presence in high concentrations in the marine environment can have adverse effects with regard to the development of marine organisms owing to the phenomenon of eutrophication. These nutrients can be transported by rivers, following leaching from arable lands, into the coastal ecosystems, and can also be produced from the degradation of organic matter after sedimentation the main process involved in sustaining primary productivity in the littoral ecosystems (Billen, 1978; Boynton *et al.,* 1980; Callender & Hammond, 1982; Hopkinson, 1987). The sediment is in fact a source of nutrients, and in many cases the magnitude of nutrient and oxygen exchange at the sediment-water interface, is sufficient to be a major component in nutrient and oxygen budget calculations (Helali, 2015). The principal factors influencing the sediment–water exchanges of iron and manganese are due to diffusion, which is considered as the main process transporting Mn^{2+} and Fe^{2+} from the sediments into estuarine water, and for nutrients the factors are sediment and the characteristics of the overlying water (Henriksen & Kemp, 1988) infaunal activity (Blackburn & Henriksen, 1983), and the nature of the deposited organic matter (Jensen *et al.,* 1988). All these elements are important for development of the biota.

The release of one element prior to the others has been attributed to the ease with which dissolved iron oxidizes and precipitates as a hydroxide in the presence of oxygen near the sediment–water interface (Van Cappellen & Wang 1996; Martin, 2005; Canavan *et al.,* 2006).

This article presents two approaches to summarize nutrient fluxes at the sediment–water interface and the associated elements included in organic matter mineralization: A theoretical approach using the pore water gradients (calculated fluxes) and an *in-situ* approach measuring the nutrient fluxes and oxygen consumption by means of benthic chambers.

In this study, we have attempted to investigate where the mineralization of the organic matter occurs below the sediment-water interface, how it influences the contents of the overlying water through its association with the nutrient elements, oxygen consumption and reduction of iron and manganese, how sediment-water fluxes vary along the depth gradient, off the Mejerda River Delta, and to assess the potential environmental control over these fluxes.

This study was conducted in three distinctive depth zones in the sediments off the Mejerda River Delta, using sediment cores (15 to 70 cm) in length and three benthic chambers deployed in winter (March) and summer (August) 2012, corresponding respectively to dry and wet seasons, in Tunisia and North Africa (Helali, 2015).

Study site

Flowing 485 km from west to east, the Mejerda is the most important river in Tunisia. 80% of this river's water is used for agriculture, 16% as drinking water, and 4% for industry. Although the waters of the Mejerda River constitute the main source of supply of erosion products, the delta is also influenced by three other water flows from the Khlij canal, Ghar El Melh lagoon, and Sebkhet Ariana (Helali *et al.*, 2013), which are also connected to the marine waters (Fig. 1). This study has been conducted off the Mejerda outlet. Table 1 shows the sample locations. The seasonal variation study has been conducted only at the three points that form a radial perpendicular to the coast, across the mouth of the river (10 m, 20 m, and 40 m stations) during march 2012 (winter season) and July 2012 (summer season), corresponding to the wet and dry seasons in North Africa, respectively.

This study is a recap of the other studies carried out in the Mejerda delta, which attempted to investigate the exchange fluxes between marine waters and sediments. This zone is known for its hydrodynamics, heavily affected by a strong marine current, dependent on wind speed and direction (Brahim *et al.*, 2007), and responsible for re-suspension of the surface sediment (Helali, 2015).

Material and Methods

Pore water

The cores were retrieved by scuba divers, who used polyvinyl chloride pipes (ϕ: 50 mm and length 50 to 90 cm) and gravity corers. Placed under inert atmosphere (N_2) inside a glove box, sediment was cut into sections: In 1–2 cm slices from the core's top 20 cm, and sections of 5 cm for the rest. The pH (82862 Weilheim WTW) were measured and the sections placed in polypropylene beakers previously washed with ultrapure deionized water (Milli-Q), and then sealed under inert atmosphere. The samples were centrifuged at 3500 rpm for 20 minutes; the pore water was extracted and filtered (0.45 μm), and the porosity evaluated at 65°C from the sediment weight loss.

Benthic chambers

Benthic chambers are square-shaped boxes with a total capacity of 37.5 l, covering a sediment area of 0.25 m². Made of transparent polymethyl methacrylate (PMMA), 6 mm thick, they are equipped with a stirrer also made of PMMA, which rotates at 8 rpm. Before each sample was taken, the stirrer was switched on for 8 minutes (Helali *et al.*, 2015).

Nine 60-ml syringes placed outside the chamber and connected to the interior by a silicone pipe (3 mm diameter) were filled every 2.5 hours, triggered by an electronic timer controlling the motor mechanism. The oxygen contents inside the chamber were measured at each sampling using a WTW Profiline 197i and Ta-197 oxi electrode (Helali, 2015).
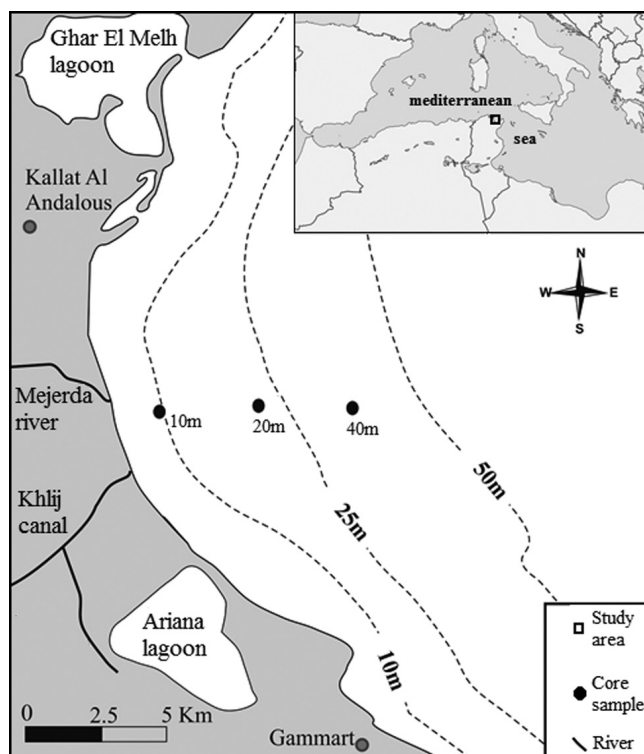

Fig. 1: Study site and sampling stations.

Table 1. Sampling locations and water depth.

Station	Latitude	Longitude	Depth (m)
10 m	37°0.468'N	10°13.821'E	10
20 m	37°0.440'N	10°16.188'E	20.5
40 m	37°0.419'N	10°17.881'E	38

Chemical analyses

Fe^{2+} concentration was determined directly from the raw sample with a Thermo Scientific ICE 3300 AA Spectrometer and Mn^{2+} was determined with a Thermo Scientific GFAAS (FS95 SOLAAR). All concentrations of the nutrient species were analyzed using a Technicon Autoanalyzer III following the analytical procedures of Mosterd (1983) for the nutrient analysis of sea water. The standard deviation of all the elements was measured from 10 replicates of the water sample taken from the same location. Table 2 presents a summary of the results.

Table 2. Standard deviation and detection limits (μM).

Element	Std deviation	Detection limit
Fe^{2+}	0.25	0.11
Mn^{2+}	1.53	0.0005
NO_3^-	0.77	0.05
NH_4^+	0.34	0.02
PO_4^{3-}	0.013	0.015

Benthic and diffusive flux calculations

Diffusive flux (J) of a dissolved component was calculated from the pore water profile according to Fick's first law: $J = -\Phi.D_{sed}\cdot\frac{dc}{dx}$, where $\frac{dc}{dx}$ represent the gradient at the sediment-water interface. To apply the law, the sediment was considered to be in a steady state. The negative sign indicated that the flux was directed to the opposite side of the concentration gradient, meaning that below the interface, as the concentration increased with depth, the flux was directed to the water column. Φ represents sediment porosity and D_{sed} represents the molecular diffusion coefficient in the sediment, while $D_{sed} = D^{sw}/\Theta^2$ with $\Theta^2 = 1 - \ln(\Phi^2)$, which is related to the tortuosity "Θ", and represents the temperature and the chemical element according to Boudreau (1997).

The benthic flux was determined from a diagram of time versus concentration. An average gradient was then selected in an attempt to best represent the average measurement points. Subsequently, the benthic flux (J_b) was determined by the equation: $J_b = \frac{dc}{dt} \times H$ (in mmol/m²/day), which $\frac{dc}{dt}$ is given in µmol/h, where "H" is the height of the benthic chamber (in m). The bottom water content is the same as in the benthic chamber at t = 0 hours, for all nutrient profile concentrations.

Results

Oxygen

As the oxygen content disappeared a few millimeters below the sediment–water interface, the oxygen flux was determined solely by direct measurement, using benthic chambers. A gradual decline in concentration was observed in both March and August at all three stations (Fig. 2). After 24 hours, the oxygen concentrations remained above 0.13 mM and the incubated waters were still oxic. In the sediments in the waters facing the Mejerda Delta, oxygen consumption was found to be higher in winter than in summer, the difference being greater at the 10-m station where the flux was 8.44 mmol/m²/day in winter and 1.72 mmol/m²/day in summer (Table 3).

Dissolved manganese and iron

The maximum content of Mn^{2+} in the pore water did not exceed 22 µM at the three stations. The Mn^{2+} concentration increased just below the sediment-water interface, and therefore, the profiles showed a strong gradient there. The Mn^{2+} peak occurred at different levels, about 3 cm in March and only at 1 cm in August (Fig. 3). Beyond a 10-cm depth, the Mn^{2+} concentration decreased rapidly (below detection limits). The benthic flux of manganese was higher at the 20-m and 40-m stations (160 and 150 µmol/m²/day), respectively, while it was only 90 µmol/m²/day at the 10-m station (Table 3).
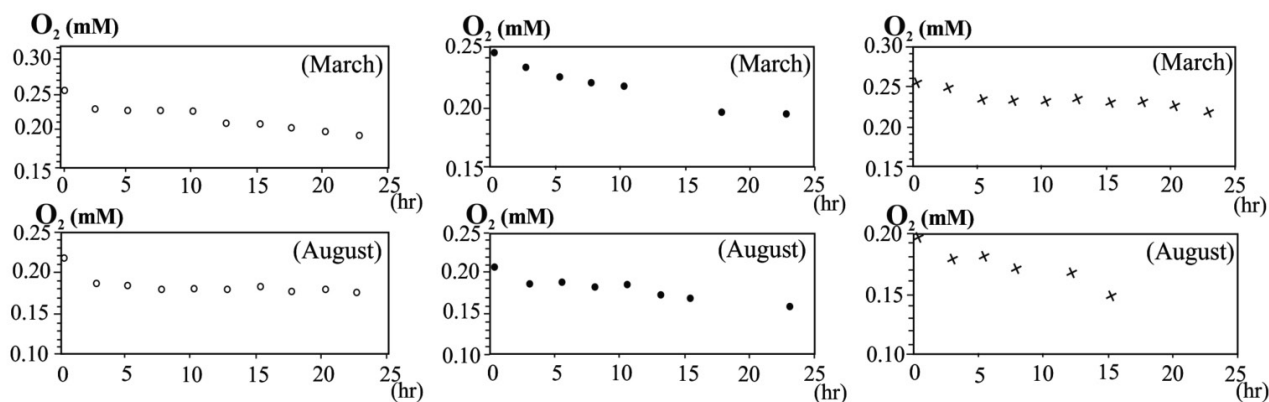

Fig. 2: Evolution of dissolved oxygen during *in-situ* incubation experiments.

Table 3. Oxygen consumption and benthic fluxes at the sediment–water interface.

Season	March			August		
Station	10 m	20 m	40 m	10 m	20 m	40 m
O_2 (mmol/m²/day)	8.44	7.87	2.3	1.72	6.72	10.36
Fe^{2+} (µmol/m²/day)	230	384	220	192	192	-38
Mn^{2+} (µmol/m²/day)	86	120	170	96	160	150
NO_3^- (µmol/m²/day)	13.44	9.6	19.2	**	**	**
NH_4^+ (µmol/m²/day)	420	96	192	3406	1728	3264
PO_4^{3-} (µmol/m²/day)	96	182.4	57.4	-19.2	17.28	20.16

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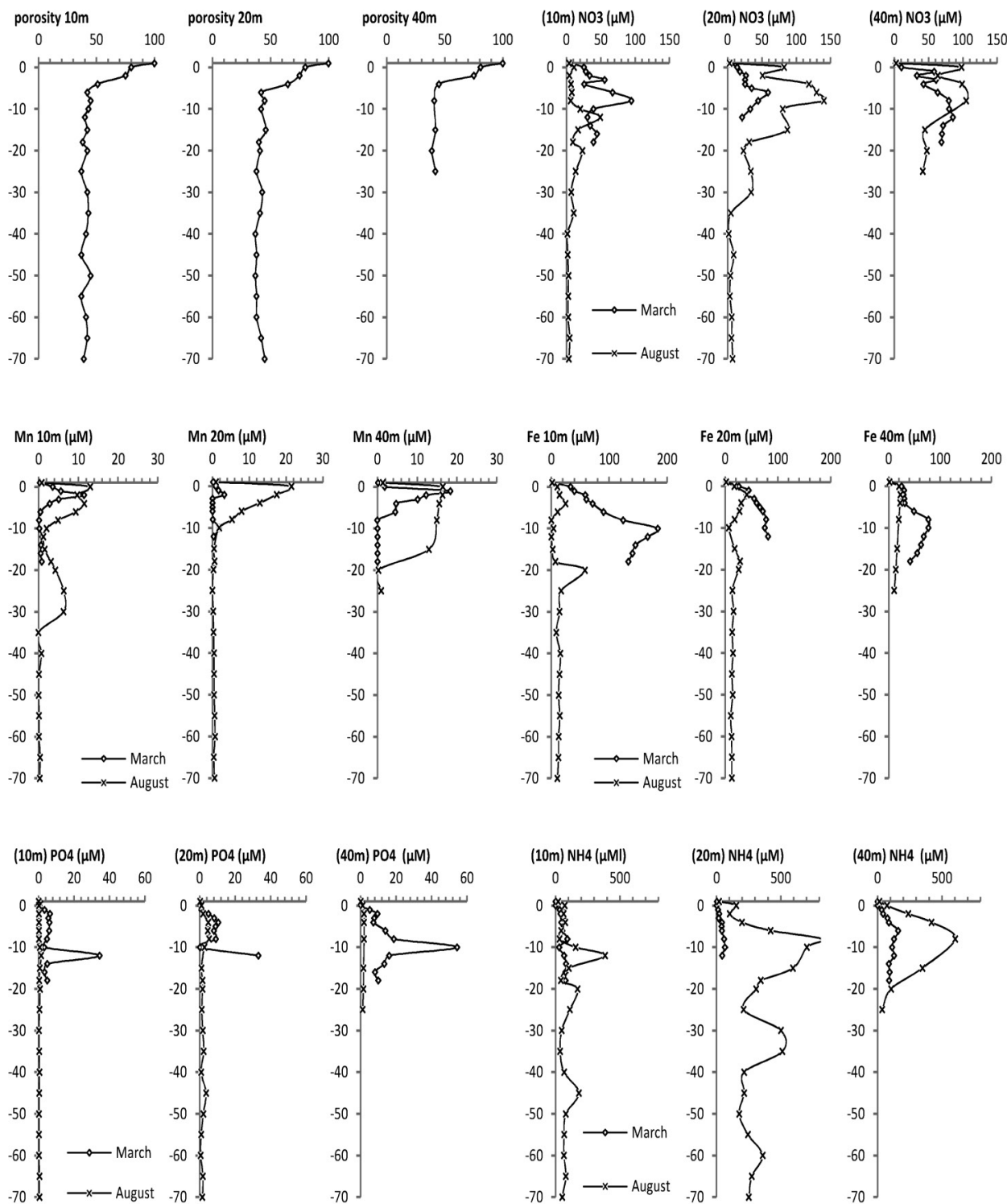*Medit. Mar. Sci., 16/3, 2015, 636-643*

Fig. 3: Pore water profile of porosity, Fe^{2+}, Mn^{2+}, NO_3^-, NH_4^+, and PO_4^{3-}.

The Fe^{2+} content varied greatly between seasons (Fig. 3). In March, the concentration varied between 80 µM at the 20- and 40-m stations and 200 µM at the 10-m station. In August, the highest value did not exceed 50 µM. Most Fe^{2+} variations occurred in the first 10 cm below the sediment-water interface (Fig. 3). As the concentrations of Fe^{2+} were very low in the water column (3 µM), an important gradient was observed just below the sediment–water interface. The calculated fluxes showed that the sediment was a source of Fe^{2+} for the water column, especially at the 10- and 20-m stations. The maximum seasonal difference was observed at the 10-m station, where the diffusive flux was 8.65 µmol/m²/day in March, but only 4 µmol/m²/day in August. There was no clearly established gradient below the sediment-water interface in the 40-m station during the two seasons, the flux was considered to be almost

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zero. Variations in the benthic fluxes of iron were slightly greater in March: 230, 384, and 220 µmol/m²/day at the 10-m, 20-m, and 40-m stations, whereas, they were 190 µmol/m²/day at the 10-m and 20-m stations in August and there were reversed fluxes (-38 µmol/m²/day), in the 40-m station.

Nitrates

The lateral variation of nitrate content at the base of the water column was noted to be high for each of the two seasons. The highest content (4 µM) was recorded in August at the 10-m station, and 3.32 and 2.42 µM, respectively, at the 20- and 40-m stations. The pore water profiles showed a sharp increase just below the sediment-water interface, therefore, no clear evolution appeared. At the 10-m station, the nitrate content was higher in winter (100 µM) than in summer (50 µM). At the 20-m station, the highest level of nitrate (about 150 µM) was recorded during summer, whereas, the nitrate level during winter was 60 µM. At the 40-m station, seasonal variations were relatively low and a maximum nitrate concentration of 80 to 100 µM was recorded (Fig. 3). The concentration gradients showed that NO_3^- was produced below the sediment–water interface, and the diffusive fluxes in winter were estimated to be 18, 15, and 25.8 µmol/m²/day at the 10-, 20- and 40-m stations, respectively (Table 4). The benthic fluxes of nitrates were measured only during winter, which were positive at all three stations: 13.44, 9.6, and 19.2 µmol/m²/day at the 10-, 20-, and 40-m stations, respectively (Table 3).

Ammoniacal nitrogen

All profiles of NH_4^+ showed an increase in concentrations below the sediment–water interface. This was more marked in summer, leading to a high seasonal variation in diffusive fluxes. The layer of NH_4^+ production varied little between the two seasons, it occurred between 5 and 8 cm in winter and 10 and 12 cm in summer, depending on the station (Fig. 3). In August, the diffusive fluxes of NH_4^+ were, on an average, 230 µmol/m²/day, while they were only 32 µmol/m²/day in March (Table 4).

Al though NH_4^+ is the main form of nitrogen discharged from the sediment into the water column, the benthic fluxes off the Mejerda Delta are relatively small, especially in winter: They are 96 to 420 µmol/m²/day (Table 3). Seasonal variation in the benthic flux is consistent with that observed for the diffusive flux, where the NH_4^+ concentrations are much higher in summer. Benthic fluxes are much higher in the summer, from 1728 to 3400 µmol/m²/day, while in the winter the benthic fluxes are much lower, 420, 96, and 192 µmol/m²/day, at the 10-, 20-, and 40-m stations, respectively (Table 3).

Phosphorus

The maximum phosphorus production was found to be 10 cm below the sediment–water interface in March, (30 µM at the 10- and 20-m stations, and > 50 µM at the 40-m station). In August, the production that occurred at a 5-cm depth was much lower than that observed in winter (5.5 µM at 20 m and 2 µM at 40 m). No gradient was visible below the sediment–water interface at the 10-m station, as the phosphorus content remained stable and equal to that at the base of the water column (Fig. 3). Similar to NH_4^+ fluxes, the phosphorus fluxes calculated were lower than those measured (benthic flux). They in fact represented only 0.4 to 4.28% of the benthic flux in summer and 2.4 to 4.4% in winter. The benthic fluxes of phosphorus were almost always positive; they were greater in winter, ranging from 96 to 180 µmol/m²/day, whereas, in summer they did not exceed 20 µmol/m²/day (Table 3).

Discussion

Oxygen: Several studies have shown that the evolution of oxygen in the incubation water is exponential, with a sharp drop during the first hours, followed by a gradual decline. This is due to oxidation of the sedimentary particles re-suspended during installation of the benthic chamber (Added, 2002; Pamatmat & Banse, 1969) and oxygen consumption by microorganisms in the water where dark chambers are used (Added, 2002), which is probably not the case in the present study. This trend proved that oxygen consumption at the sediment–water interface is lower than expected. In comparison, after 24 hours of incubation in the Ghar El Melh Lagoon, the oxygen concentration decreased from 0.17 to 0.045 mM (Oueslati, 2011). Oxygen consumption below the sediment-water interface was dependent on various biogeochemical processes, such as, aerobic degradation of organic material, bioturbation and irrigation to the sediment, and precipitation of mineral particles through pore water oxidation.

The benthic chambers used in the present study were transparent, which should have led to a different evolution in flux during the daytime incubation period. This, however, was not the case, confirming that photosynthesis was probably of no greater importance in the changes in oxygen fluxes at the sediment–water interface than the various processes of oxygen consumption. Off the shoreline of the Mejerda Delta, the flux measured for over 24 hours was the result of two opposing processes, namely photosynthesis (which was probably low due to sediment re-suspension)

Table 4. Diffusive fluxes of Fe²⁺, Mn²⁺, and nutrients (µmol/m²/day) at the sediment-water interface.

Season	March			August		
Station	**10 m**	**20 m**	**40 m**	**10 m**	**20 m**	**40 m**
Fe²⁺	8.65	9.38	0	4.1	10.62	0
Mn²⁺	2.57	0.93	14.63	14.22	17.9	13
NO₃⁻	17.2	14.92	25.87	15	179.15	212
NH₄⁺	22	14.8	60	5.97	236	241
PO₄³⁻	2.3	2.53	2.53	-0.078	0.74	0.3

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and the chemical and biological oxygen demand. In the present study, the measured fluxes during 24 hours of incubation (Fig. 2, Table 3) represented components of the diurnal and nocturnal flux; It appeared that in the conditions of our study area, turbidity was present, probably due to the sediment-water interface re-suspension and suspended matter originating from the Mejerda River (Helali, 2015).

Manganese and iron: Mn^{2+} is produced below the sediment-water interface; this is one of the different anaerobic processes of the overall scheme in early diagenesis. Manganese is found in its oxide form (MnO_2) as marine water is oxygenated; the reduction of this mineral is the main cause of increase in the Mn^{2+} content in the pore water, according to the reaction:

$$OM + 2x\ MnO_2 + (3x + y - 2z)CO_2 + (x + y - 2z)H_2O \rightarrow 2x\ Mn^{2+} + (3x + y - 2z)HCO_3^- + yNH_4^+ + zHPO_4$$
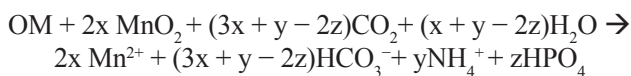
Generally, Mn^{2+} production occurs at different depths, depending on the hydrodynamic conditions and the benthic activity at the sediment-water interface. The depth ranges from a few millimeters (as for the Mejerda Delta) to some tens of centimeters, when a strong mechanical disturbance at the sediment–water interface occurs, resulting in the penetration of oxygen, causing the layer of manganese oxide reduction to descend, as in the Ghar El Melh Lagoon (Added, 2002). In the case of the Mejerda Delta, all profiles show a downward shift in Mn^{2+} production in March, without any trace of visible benthic activity at the sediment–water interface. The release of Mn^{2+} prior to Fe^{2+} has been attributed to the ease with which dissolved Fe, after migrating upward by molecular diffusion, oxidizes in the presence of oxygen near the sediment–water interface and precipitates as hydroxides (Van Cappellen & Wang, 1996; Martin, 2005; Canavan et al., 2006), according to the following reactions:
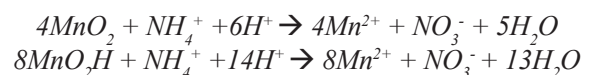
$$2Fe^{2+} + MnO_2 + 4H_2O \rightarrow Mn^{2+} + 2Fe(OH_3) + 2H^+$$
$$Fe^{2+} + 0.25O_2 + 2HCO_3^- + 0.5H_2O \rightarrow Fe(OH_3) + 2CO_2$$
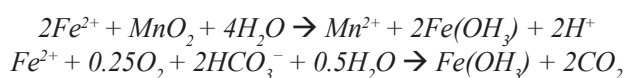
The redox conditions that characterize the delta sediment are not sufficiently reduced to permit the formation of such minerals. The reduced Mn^{2+} contents in the deep layers of the sediment are the result of the element's diffusion (Helali et al., 2015). Diffusion also takes place upwards, with the release of Mn^{2+} into the water column, where it is probably re-oxidized by the dissolved oxygen (Helali et al., 2015). It appears that the decrease in the Fe^{2+} concentration at the lowest depth of the sediment core is due to the diffusion of this metal and not because of the formation of a mineral complex. As for Mn, the reason is that the delta sediment functions on a non-stationary regime and is, therefore, unable to precipitate minerals (Helali et al., 2015).

Nitrates: NO_3^- concentrations are higher, especially in winter, although nitrates are not the most important dissolved inorganic nitrogen components in regard to the redox conditions in the sediment off the Mejerda outlet (Helali, 2015).

Nitrates are a product of aerobic oxidation of the organic nitrogen:

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e \rightarrow NO_2^- + H_2O \rightarrow$$
$$NO_3^- + 2H^+ + 2e$$
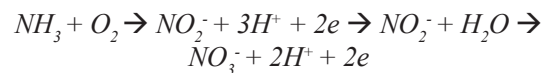
Nitrification is then an aerobic process that can only take place in oxic zones and can take place below the oxic layer; this is the case of the sediment in our study area, and this is provided by different mechanisms: Temperature, NH_4^+ content, microorganism activity, and so on (Hensen et al., 2003). Yet we observe no infaunal activities below the sediment-water interface at the three stations, which could explain oxygen transport. The presence of nitrates and nitrites below the oxic layer may thus be the result of the diffusion of nitrates/nitrites and/or the result of anoxic production (chemical production) (Helali, 2015). Some irregularity in the production of NH_4^+ suggests the simultaneous existence of an NH_4^+ producer process (degradation of organic matter) and another diagenetic process responsible for consumption. NH_4^+ may be oxidized to nitrate in the presence of manganese and iron oxyhydroxides (Luther & Popp, 2002; Chaillou et al., 2003) as follows:

$$4MnO_2 + NH_4^+ + 6H^+ \rightarrow 4Mn^{2+} + NO_3^- + 5H_2O$$
$$8MnO_2H + NH_4^+ + 14H^+ \rightarrow 8Mn^{2+} + NO_3^- + 13H_2O$$

Nitrate levels are relatively strong in a marine environment; the production of nitrates is not limited to the oxic zone and continues further down in the sediment, below the areas where reduction of manganese oxides and iron hydroxides occur (Fig. 3). In general, high levels of nitrates are observed in environments with the oxic zone widely spread at the depth (Added, 2002; Helali, 2015). This scheme may strengthen the hypothesis that in the sediments off the Mejerda Delta, the production of nitrates is not only dependent on the primary reactions of early diagenesis, but also on a set of chemical processes that occur well below the reduction zone of iron and manganese oxyhydroxides (Helali et al., 2015). Furthermore, this may also explain the relatively high levels of nitrates observed in the present study at the different stations during the two seasons.

Ammoniacal nitrogen: It has been reported that in the northern part of the Mejerda Delta, NH_4^+ contents range from 100 to 400 µM, increasing below the sediment–water interface (Essoni, 1998). Elsewhere in the Gulf of Tunis, the highest concentrations (200 to 800 µM) were recorded south of the Mejerda (Essoni, 1998). In Ghar El Melh Lagoon, the behavior of NH_4^+ is similar to that observed in the sediment off the delta shore. According to season a variable increase is observed just below the sediment–water interface, with the highest recorded levels reaching 300 µM (Added, 2002). NH_4^+ production is an anaerobic process originating in nitrates as follows:

$$NO_2^- + 8H^+ + 6e \rightarrow NH_4^+ + 2H_2O$$
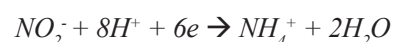
NH_4^+ can only be formed under specific conditions such as an oxygen minimum of 100 µM and Eh < 260 mV (Fernex et al., 1989) which is the case in the sediment off the Mejerda delta (Helali, 2015). This element is also a

product of the anaerobic mineralization of organic matter. Variation in the NH_4^+ content is also under the influence of the adsorption phenomena. Both the measured (benthic) and calculated (diffusive) fluxes always move from the sediment into the water column. NH_4^+ is produced via degradation of organic matter occurring below the sediment–water interface; positive fluxes may result when it is diffused, passing upwards into the water column. Diffusive fluxes, though, are lower than the benthic fluxes measured directly above the sediment–water interface, representing only 0.17 to 13% of benthic fluxes in summer and 5 to 31% in winter. Thus, many of the chemical reactions provoking the release of NH_4^+ take place just below the sediment–water interface.

Phosphorus: PO_4^{3-} is also a product of the mineralization of organic matter below the sediment-water interface by different processes: Aerobic respiration, denitrification, reduction of MnO_2, $Fe(OH)_3$, sulfates, and methanogens (Van Capellen & Wang, 1996; Canavan *et al.,* 2006). Similar to NH_4^+, all fluxes of phosphorus (benthic and calculated) are directed to the water column.

PO_4^{3-} is a sensitive element that can be easily eliminated by chemical processes, such as, precipitation and adsorption (formation of authigenic iron and calcium minerals) (Barbanti *et al.,* 1995), although this is not the case in the Mejerda delta (Helali *et al.,* 2015).

Calculated fluxes of PO_4^{3-} are lower than the benthic fluxes, and they represent only 0.4 to 4.4% of the calculated fluxes. This is probably due to the rule of physical processes acting on the seafloor (probably wave action and river currents acting in the Mejerda outlet). This finding has been reported in several studies on phosphorus exchange (Forja & Gomez Parra, 1998; Callender & Hammond, 1982).

Benthic and diffusive fluxes acting in some direction, the phosphorus released from the sediment during the degradation of organic matter will diffuse into the water column and the sediment off the delta will then act as a source of this element to the overlying water. Despite relatively similar starting concentrations between the three stations, the diffusive flux of phosphorus is different, showing that its rate of release into the water column is related to the degree of decomposition of organic matter at the outset (Forja *et al.,* 1994; Ponce *et al.,* 2010).

The diagenetic sequence off the Mejerda outlet is the same at all the studied stations. Figure 4 represents the sequence and it consists of: An aerobic degradation of a few-millimeter thickness that can only be assumed below the water–sediment interface, followed by different anaerobic mechanisms in the following order: Reducing oxides of manganese and reduction of iron hydroxides, within 15 cm, probably followed by sulfate-reducing (Fig. 4). In parallel there is a nitrate production from bacterial and chemical processes and phosphate and ammonium production due to bacterial degradation. Seasonal variation provokes a migration of the depth of various layers when production of dissolved elements occurs. This is probably due to the variation in the agitation of the marine water off the Mejerda outlet and the re-suspension of the surface layer of the sediment. This process is also responsible for the increase in the concentration of some elements, particularly in winter. This variation is characteristic of the marine environment and would be the result of degradation of the freshly deposited organic material on the sea floor.

Conclusion

The diagenetic sequence in the Mejerda River Delta for all studied stations showed the same trend. First, aerobic mineralization, a few millimeters thick, which can only be assumed below the sediment–water interface, when oxygen consumption is not as intense as that observed in other similar maritime areas. This is then followed by various anaerobic mechanisms: Biological and chemical production of nitrates, which explains the increase in nitrate levels and their production far below the sediment–water interface. The reduction in manganese oxides, then a reduction in iron hydroxides to a depth of 15 cm leads to a significant flux of Fe^{2+} and Mn^{2+} from the ferruginous and manganous zones of the sea floor into the lower water column. Surface sediment off the Mejerda delta can be considered as a source of dissolved iron and manganese, as illustrated by the pore water profiles. The release of phosphorus and ammoniacal nitrogen from the sediment into the water column is attributed to the mineralization of organic matter. The ammoniacal form (NH_4^+) is the most important form of nitrogen. Although the phenomena responsible for the release of these elements have varied little between the coastal and offshore areas, the intensity has appeared to increase during winter, and in the absence of
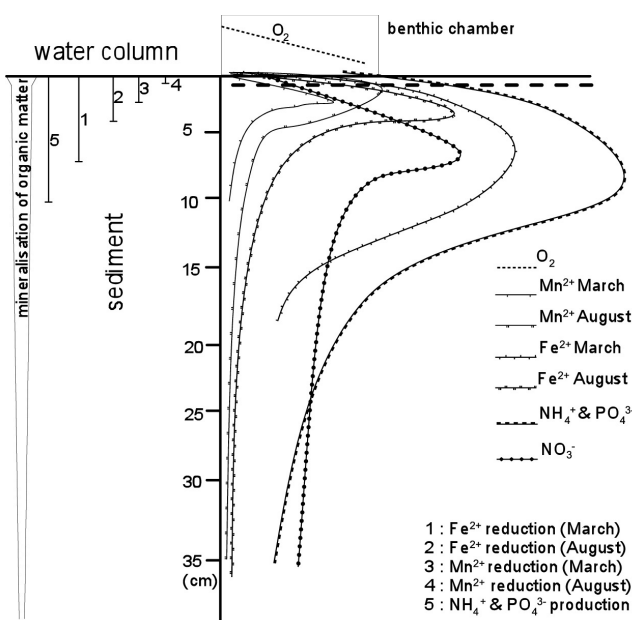

Fig. 4: General diagenetic scheme occurring off the Mejerda Outlet.

any trace of biological activity this may be due to the agitation of the environment under wave action, which could be the main factor accelerating nutrient diffusion.

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