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**In vitro simulation of oscillatory redox conditions in intertidal sediments: N, Mn, Fe,  
and P coupling.**

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## **Abstract**

In coastal environments, oscillating redox conditions represent a functional state affecting organic matter mineralization. Such transient diagenetic processes remain difficult to study in situ, and we therefore designed a specific reactor to provide experimental results that are environmentally relevant in this context. Here, we present the results of two independent experiments carried out with sediment having contrasting Fe, Mn contents, collected from a coastal tidal lagoon (the Arcachon bay) and a mesotidal estuary (Adour river). Sediment and overlying water were mixed to form slurries that were submitted to redox oscillations to assess the diagenetic mechanisms that affect N, P, Fe, Mn, and S. Changing from anoxic to oxic conditions, we observed a rapid oxidation of dissolved Fe(II) and dissolved inorganic phosphorus (DIP) was apparently trapped by the newly formed Fe-oxyhydroxides (Fe-ox). DIP was totally titrated in the coastal lagoon sediment, but not in estuarine sediment, where the initial amount of Fe available was lower. In both experiments, Mn(II) was only slowly oxidized during the oxidation events and a major part of Mn(II) was adsorbed on new Fe-ox. In coastal lagoon sediment, ammonium remained constant in oxic conditions while nitrate was produced from organic-N mineralization. On the contrary, in estuarine sediment, ammonium was quantitatively oxidized to nitrate. When the conditions became anoxic again, direct reduction of nitrate to ammonium occurred in coastal lagoon sediment. Anaerobic production of nitrate occurred in estuarine sediment, probably because Mn-oxides (Mn-ox), which had a high concentration, acted as an oxidant for ammonium. Consequently, nitrate production prevented Fe(II) accumulation. The Mn-N-Fe coupling outlined here is an apparent indirect oxidation of Fe(II) by Mn-ox through anaerobic nitrification (with Mn-ox) and denitrification (with Fe-ox). This coupling also implied P availability because of the strong control of P by Fe. These experimental results show that nutrient dynamics in oscillatory redox environments such as the estuarine turbidity zone, bioturbated sediment, or tidal permeable sediments highly depends on Mn-and Fe-ox availability.

Keywords: benthic biogeochemistry; redox oscillation; nutrients; coastal sediments; iron oxide; manganese oxide

## 1. Introduction

The successive use of electron acceptors that yield the highest amount of free energy in the terminal step of bacterial oxidation of organic matter partly explains the vertical stratification of redox compound distribution below the sediment water interface (Froelich et al., 1979). However, the steady state hypothesis implying that a parcel of sediment deposited under oxic conditions moves to suboxic conditions, and then definitively to anoxic conditions through burial below the oxygen penetration depth is unwarranted in most aquatic environments. Indeed, sediments are subjected to redox oscillations due to advective transport of particles and solutes, migration of the redox front, or a combination of both processes. Consequently, considerable effort has been devoted to understanding diagenetic processes under transient redox conditions (Sundby, 2006).

Redox oscillations due to advection of sediment particles have been described in several cases, such as fluid mud mobilization and bioturbation. Mobile fluid muds, which can be found in the Amazon deltaic plume and in the turbidity maximum zone of estuaries, experience oxygenation during resuspension of particles (Aller, 1998; Abril et al., 2000). Oxygen inputs allow a new stock of nitrate and reactive iron and manganese oxides to be regularly built, which eventually enhances the mineralisation of organic matter (Sun et al., 1993, Aller, 1994; Abril et al., 2010). Bioturbation due to the mixing activity of infaunal macrobenthos (Rhoads, 1974; Aller, 1982) significantly affects the distribution of biogeochemical species inside the sediment as well as their fluxes at the sediment-water interface (e.g. Yingst and Rhoads, 1980; Aller, 1982; Blackburn, 1988; Meysman et al., 2006). Organic material and electron acceptors are thus redistributed in the sediment column, generating redox oscillation of sediment parcels. (Aller, 1994, Sun et al., 2002; Gilbert et al., 2003, Volkenborn et al., 2010).

In coastal environments, excursion of redox fronts below the sediment-water interface occurs at different time scales. The oxygen penetration depth can change everyday due to photosynthetic and respiration activity of biofilms or macrophytes at the surface of sediments (Pringault et al., 2005; Sundby et al., 2003; Frederiksen and Glud, 2006). It may also migrate toward the sediment surface after pulses of labile organic matter supply (e.g., Gobeil et al., 1997; Katsev et al., 2006; Glud, 2008 and references therein). In permeable sediments, redox conditions also vary according to wave action, tidal pumping, and bottom topography (Ziebis et al., 1996; Precht et al., 2004, de Beer et al., 2005; Cook et al., 2007 ; Deborde et al., 2008a). In such sediments, oxygen can be advected deep into the sediment while outwelling may also force anoxic porewater right to the sediment surface (Huettel et al., 1998; Ibanhez and Rocha, 2016).

Examples cited above suggest that in almost all the modern sediments, particulate redox-sensitive phases are in contact with either oxic or reduced reactive dissolved species. Among redox-sensitive phases, particulate reactive Mn- and Fe-(oxyhydr)oxides (Mn-ox and Fe-ox) play a central role in sedimentary biogeochemical reactions, because they are involved in the benthic cycle of major nutrients such as N and P. Among the many possible redox reactions, there is the oxidation of ammonia to di-nitrogen by Mn-ox in the presence of oxygen (Luther et al., 1997), the oxidation of sulphide to sulphate and ammonia to nitrate by Mn-ox in the absence of oxygen (Aller and Rude, 1988; Hulth et al., 1999, Anschutz et al., 2000; 2005; Mortimer et al., 2004), and the oxidation of Fe(II) to Fe-ox by nitrate (Hyacinthe et al., 2001) or by Mn-ox (Hartmann, 1985 ; Anschutz and Blanc, 1995 ; Dellwig et al., 2010). Iron plays an important role in the cycle of phosphorus since dissolved phosphate can be strongly sorbed or co-precipitated with Fe-ox and be removed from sediment pore water (e.g. Krom and Berner, 1980), while Fe-ox reductive dissolution releases stored phosphate (e.g., Sundby et al., 1992). Therefore, redox oscillations may result in a complex sequence of

reactions that make the predictive modelling of N and P behaviour difficult (Katsev et al., 2006).

Redox oscillations have been studied mostly in order to assess their impact on organic carbon and nitrogen mineralization efficiency (e.g. Aller, 1994; 1998, Abril et al., 1999, 2010; Gilbert et al., 2016). Their impact on the links between Fe/Mn cycles and N/P cycles has been largely overlooked. Microcosm experiments are useful to unravel environmental mechanisms that are hardly discriminated during in situ experiments and to assess the processes occurring under oscillating conditions (Abril et al. 2010). Here we present in detail the evolution of redox species concentrations observed in two independent experiments carried out in a specifically designed reactor. Sediment slurries with different Fe-ox and Mn-ox content were subjected to changing redox conditions under controlled conditions. The objective of this study was to compare the various diagenetic reactions occurring in these two sediments under short (days) redox oscillations with respect to their Mn and Fe contents, and especially their influence on the N and P behaviour.

## **2. Methods**

### *2.1. Sediment sampling and slurries preparation*

The sampling conditions and preparation of the slurries have been previously described in detail (Bouchet et al., 2011, 2013). Briefly, bulk superficial sediments (~5 kg, 1-3 cm depth) and overlying waters (20 L) were sampled from the two sites using protocols adapted for trace metals. Material preparation included successive cleaning with a specific detergent, 10% HNO<sub>3</sub> (Baker Analysed, JT Baker) (twice) and 10 % HCl (Baker Analysed, JT Baker) baths, rinsed with ultrapure MQ water (Quantum EX, Millipore), dried under laminar flow hood and stored in double sealed polyethylene bags until use. For the Arcachon bay, the sediment was sampled on an intertidal mudflat exposed to the atmosphere for a minimum of

12 h/day. The salinity of the overlying water sampled during high tide was 32, which is in the 22-34 salinity range observed during the year at the sampling location (Deborde et al., 2008a). For the Adour estuary, the sediment was collected on a tidal mud flat and the salinity of the overlying water was at 8. Sediment and water samples were kept at 4 °C before processing. These two sites were chosen since they are naturally subjected to redox oscillations due to bioturbation and resuspension and exhibit different contents of Mn-ox in surface sediment and different salinities. The fine fraction (<63 µm) represented more than 80% for both sediments, the organic carbon content was 4.2 and 3.2 %, and the sulphur content was 1.7 and 0.2%, in the lagoon and the estuarine sediment, respectively (Table 1). The day following sampling, sediments were homogenized and sieved to 2 mm and then to 300 µm, mixed with an appropriate volume of overlying water to reach a final volume of 20 L and introduced in the reactor (Fig. 1). The resulting slurry contained  $93 \pm 6$  and  $70 \pm 4$  g L<sup>-1</sup> suspended particle for the Arcachon bay and the Adour estuary, respectively. Suspensions were kept between 3 and 5 days under continuous stirring and N<sub>2</sub> conditions to allow the re-equilibration of the system before the beginning of the experiment.

## *2.2. Experimental setup and operating conditions*

The sediment slurries were incubated in the dark at room temperature in a custom-made set-up designed to simulate redox oscillations by maintaining them in oxic or anoxic homogeneous conditions for a determined period (Abril et al., 2010; Bouchet et al., 2011). The main component of the set-up is a 25-L gas-tight reactor made of Pyrex set on a magnetic stirrer (Gilbert et al., 2016), which allow flushing the slurries to either air or O<sub>2</sub> free gas through an immersed glass frit bubbler (Fig. 1). Gas flushing of the whole slurry prevented CO<sub>2</sub> accumulation and drastic pH changes. The slurry was continuously stirred by a central Teflon-coated magnetic stirring bar. This design prevented the sedimentation of particles,

which would have created an anoxic sedimentary environment in periods when oxic conditions were sought.

Probes for pH/temperature (Metrohm 713 pH-meter) and a polarographic oxygen electrode (YSI 5000, calibrated in water-saturated air) were located in the lower part of the reactor. An outlet pipe equipped with a Teflon lined glass valve also allowed discrete samples to be collected at high frequency using gas tight syringes to avoid any alteration from the ambient air.

For each sample, about 60 mL slurry was removed from the reactor, immediately transferred to a polypropylene tube flushed with N<sub>2</sub> and centrifuged (under N<sub>2</sub> or ambient atmosphere according to the period) for 15 min at 2280 g. Supernatant fluids were filtered through 0.2 µm acetate cellulose syringe filter, split into several aliquots and acidified with a 1% equivalent volume of ultrapure concentrated HCl for dissolved Fe, Mn and inorganic phosphorus determinations. These subsamples were kept refrigerated in the dark until analysis. Samples for ammonium, nitrate, and nitrite analysis were transferred to polyethylene vials and frozen immediately. The residue was immediately frozen at -20°C for solid-phase composition analyses.

Oxic or anoxic conditions were obtained by occasionally purging the gas and water phases with either air or N<sub>2</sub>. Both experiments started with anoxic conditions. For the Adour estuary sediment, stable anoxic conditions were maintained for 4 days. This period was followed by 6 days of oxic conditions with a mean oxygen saturation of 40% (111 µM). The sediment was anoxic again between day 10 and day 12. For the Arcachon lagoon sediments, the initial anoxic period was of 11 days, but a leak occurred on day 4 so that the slurry became accidentally oxic for a few hours. At day 11, the slurry was purged with air and it was maintained oxic for one week, except at day 14, when the slurry became temporarily anoxic because of a magnetic stirred failure. Although it was difficult to maintain stable oxic



conditions because of the numerous redox reactions, most of the measured oxygen concentrations were between 30 and 150  $\mu\text{M}$ . From day 18, the slurry was kept anoxic for one week. Despite these unfortunate accidental oxidation events and the differences between incubation treatments for the two sediments, significant insight into redox cycling was obtained, as outlined in the results and discussion.

Samples were collected every 20 ( $\pm$  5) hours. The sampling time step was shortened during non-accidental redox transitions in order to assess the rates of transformations. The pH was influenced by gas flushing, but the values remained between 7.1 and 7.7 in the Arcachon slurry, and between 6.9 and 7.5 in the Adour slurry. Low values were measured during oxic periods. These 2- and 4-weeks experiments were not replicated, because we had only one 25-L reactor, and in the dynamic intertidal environments studied we would have had difficulties to find exactly the same sediment for duplicating experiments with the same sediment. All data were integrated into Microsoft Excel® software for further analyses of all experimental results. Rates of reactions were determined using the slope of linear regression of concentration evolution with time (Abril et al., 2010). Error margin were calculated with the standard deviation of the slope.

### *2.3. Analyses*

The freeze-dried solid fraction was homogenised. Particulate organic carbon (POC) was measured on freeze-dried samples by infrared spectroscopy (LECO 200 C-S analyzer) after removal of carbonates with 2M HCl from 50 mg powdered sample (Etcheber et al. 1999). An ascorbate reagent (50 g  $\text{NaHCO}_3$ , 50 g Na-citrate, 20 g ascorbic acid for 1L solution, buffered at pH 8) was used to obtain the Mn-ox content (Anschutz et al., 2005) and the most reactive Fe(III) fraction (Fe-asc) (Kostka and Luther, 1994) and the associated phosphorus (P-asc) (Anschutz et al., 1998). About 100 mg dried sample was leached with 10 mL solution for 24h

while shaking continuously at ambient temperature. The supernatant was diluted with 0.2N HCl. After each extraction, the Fe and P contents of the supernatant were determined by colorimetric procedures in a mixture of reagents adapted for each sample matrix (Anschutz and Deborde, 2016). Extracted Mn concentration was measured by atomic absorption spectrometry with external standard prepared in the same matrix.

Nitrate and nitrite were measured by flow injection analysis (FIA) according to Anderson (1979). Ammonium was analysed with the FIA method described by Hall and Aller (1992). Sulphate was measured with a nephelometric method adapted from Rodier (1976) and  $\text{Fe}^{2+}$  with the colorimetric method using ferrozine (Stookey, 1970). Dissolved sulphide was measured by a methylene blue method adapted from Cline (1969). Phosphate was measured by a colorimetric method according to Murphy and Riley (1962). Dissolved  $\text{Mn}^{2+}$  was determined by atomic absorption spectrometry. The precision of these procedures was  $\pm 5\%$ . Detection limit (DL) was 1  $\mu\text{M}$ , 0.05  $\mu\text{M}$ , 0.02  $\mu\text{M}$ , and 0.3  $\mu\text{M}$  for  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , phosphate, and dissolved Fe(II), respectively. Ammonium and sulphate DL was 10  $\mu\text{M}$ .

### **3. Results**

#### *3.1. Concentrations in the solid phases*

Concentrations measured in the solid fraction did not change significantly during both incubations. The mean value of particulate organic carbon was 3.2 and 4.2 wt% in the Adour estuary and Arcachon lagoon sediments, respectively. The mean value of iron extracted with ascorbate was 180  $\mu\text{mol g}^{-1}$  in the Arcachon lagoon. Phosphorus content associated with this fraction was at 11  $\mu\text{mol g}^{-1}$ . The respective values for the Adour estuary sediment were 47 and 9.8  $\mu\text{mol g}^{-1}$ . The manganese oxide content differed greatly between the two sediments, its concentration was 9.8  $\mu\text{mol g}^{-1}$  in the Adour estuary sample and 1.4  $\mu\text{mol g}^{-1}$  in the Arcachon lagoon sample (Table 1).

### 3.2. Dissolved Fe and P behaviour

Dissolved reduced solutes were initially present in both dissolved fraction (Fig. 2) but lagoon sediments were much more concentrated in dissolved iron (II) and ammonium than estuarine sediments. The concentration of dissolved  $\text{Fe}^{2+}$  was close to  $400 \mu\text{mol L}^{-1}$  ( $\mu\text{M}$ ) in the lagoon slurry and at about  $50 \mu\text{M}$  in the estuarine slurry. As soon as the slurries became oxic, dissolved iron concentrations collapsed to values close to zero at a rate above  $2000 \mu\text{M day}^{-1}$ . In the Arcachon slurry,  $\text{Fe}^{2+}$  concentration then remained below  $20 \mu\text{M}$  during the oxic period while it remained below  $3 \mu\text{M}$  in the Adour slurry. Low and variable concentration of dissolved iron was observed during the accidental oxidation that occurred between days 4 and 7. When anoxic conditions were recovered at the end of the experiments dissolved Fe increased regularly at a slow rate of  $29 \pm 1 \mu\text{M day}^{-1}$  after the day 22 in the lagoon sediment whereas it remained low in the estuarine sediment.

Initial dissolved inorganic phosphorus (DIP) concentrations were of the same magnitude in both slurries ( $12 - 16 \mu\text{M}$ ). DIP dropped to a value close to 0 ( $0.2 \mu\text{M}$ ) in the lagoon sediment when dissolved oxygen was introduced in the reactor, and increased again when reduced conditions were recovered, but still remained below  $2 \mu\text{M}$ . The concentration was increasing at a rate of  $0.7 \pm 0.1 \mu\text{M day}^{-1}$  during the first 2 days and then  $0.1 \mu\text{M day}^{-1}$ . DIP also decreased right after oxygen input in the estuarine sediment, but the concentration remained at about  $1 \mu\text{M}$ . After day 6, DIP concentrations remained between 2 and  $3 \mu\text{M}$ , even after the anoxic-oxic redox transition.

### 3.3. Dissolved nitrogen species cycling

In the Arcachon lagoon sediments, ammonium concentration was  $684 \mu\text{M}$  at the beginning of the experiment (Fig. 2). It increased at a rate of  $22 \pm 1.5 \mu\text{M day}^{-1}$  from day 0 to day 10, and at a relatively similar rate of  $26 \pm 1.4 \mu\text{M day}^{-1}$  between day 22 and day 25,

during the well-established anoxic periods. During the 8 days of oxic conditions, it remained constant at a value around 1000  $\mu\text{M}$  but then its production peaked at a rate of  $52 \pm 14 \mu\text{M day}^{-1}$  during the subsequent 3.5 days. The mean ammonium production rate was thus  $23 \mu\text{M day}^{-1}$  over the entire incubation period. In the estuarine slurry, the initial ammonium concentration was 250  $\mu\text{M}$ , and it increased at a rate of  $12 \pm 1.4 \mu\text{M day}^{-1}$  until oxic conditions started. Then, it dropped at a rate of  $200 \pm 10 \mu\text{M day}^{-1}$  to values below 10  $\mu\text{M}$  and remained so until the beginning of the next anoxic period (day 10), when it increased again at a rate of  $34 \pm 4 \mu\text{M day}^{-1}$  to a value that remains constant at 50  $\mu\text{M}$  after day 11.

During the initial and final anoxic periods, nitrate+nitrite ( $\Sigma\text{NO}_3$ ) concentrations remained below the detection limit of 0.3  $\mu\text{M}$  in the Arcachon lagoon sediment. During the oxic period,  $\Sigma\text{NO}_3$  laterly increased at a rate of  $44 \mu\text{M day}^{-1}$  (nitrite accounting for 25 to 50 %) but it vanished very quickly at a rate of  $89 \pm 6 \mu\text{M day}^{-1}$  when the conditions became anoxic again. In the estuarine sediment experiment,  $\Sigma\text{NO}_3$  concentrations ranged between 7 and 13  $\mu\text{M}$  during the initial anoxic period. Shortly after the oxic period started, nitrate reached a value of 310  $\mu\text{M}$  at a rate of  $243 \pm 22 \mu\text{M day}^{-1}$  and then remained constant at about 250  $\mu\text{M}$ . During the last anoxic period, nitrate concentrations did not collapse and oscillated between 216 and 470  $\mu\text{M}$ .

#### 3.4. *Dissolved Mn*

In the lagoon slurry, dissolved Mn evolved with little variation from an initial concentration of 62  $\mu\text{M}$  to a final value of 50  $\mu\text{M}$ . At the beginning of the oxic period, concentrations decreased rapidly at a rate of  $27 \pm 10 \mu\text{M day}^{-1}$  and then at a slower rate of  $0.7 \pm 0.2 \mu\text{M day}^{-1}$  to a minimal value of 36  $\mu\text{M}$ . After the establishment of anoxic conditions at day 21, dissolved Mn increased again to reach 51  $\mu\text{M}$  the day 24. The estuarine slurry showed a relatively constant concentration of dissolved Mn of 93  $\mu\text{M}$  during the initial anoxic period.

At the onset of oxic conditions Mn concentration abruptly decreased by 10  $\mu\text{M}$  and then reached a value below 1  $\mu\text{M}$  in 4 days at a mean rate of  $22 \pm 2.5 \mu\text{M day}^{-1}$ . After the recovery of anoxic conditions, dissolved Mn concentration increased again at a rate of  $10 \pm 1 \mu\text{M day}^{-1}$  to reach a plateau at 8  $\mu\text{M}$  after a few hours.

### 3.5. *Dissolved sulphur species*

Free sulphide was never detected under any conditions in both experiments (detection limit 2  $\mu\text{M}$ ). Mean sulphate concentration were 25 mM at the beginning of the Arcachon sediment experiment. It increased to a concentration of 27 mM as the slurry became oxic. Adour estuary experiment showed the same pattern with an initial concentration of 6 mM and a value that reached rapidly a mean and a constant value of 6.9 mM after the oxygenation of the slurry.

## 4. Discussion

### 4.1. *Similarities and differences in the initial solid composition of the two sediments*

Both sediment contained high concentrations of organic carbon with measured values typical of the sampling location (Deborde et al., 2008b; Mouret et al., 2016; Point et al., 2007). The water/sediment ratio was in the same range for both experiments with a suspended particulate matter concentration of  $93 \pm 6$  and  $70 \pm 4 \text{ g L}^{-1}$  for the Arcachon lagoon and the Adour estuary, respectively. Differences occurred in the ascorbate extracted fractions; ascorbic acid buffered at pH 8 is known to extract selectively only the most reducible fraction of Fe-ox (Kostka and Luther, 1994; Hyacinthe and Van Cappellen, 2006), that carries the major part of P associated with Fe(III) phases (Anschutz et al., 1998), but also dissolves almost all the Mn(III,IV) phases (Anschutz et al., 2005; Mouret et al., 2009). Both sediments contain high concentrations of Fe-asc, which is normal for the Arcachon lagoon because the watershed of the main river that feeds the lagoon consists of a Quaternary sandy soils

enriched in iron oxides (Buquet et al., 2017). The phosphorus associated with the Fe-asc fraction showed a Fe-asc/P-asc mole ratio of 16.4 and 4.8 for the Arcachon sediment and the Adour sediment, respectively. The Arcachon value is within the ones previously published (Deborde et al., 2008b) while this is the first report for the Adour estuary sediment. The difference in Fe-asc/P-asc ratios is likely due to the size of the Fe(III) particles and the low Fe/P ratio of the Adour suggests the existence of a Fe-ox phase with very high adsorption capacity, i.e. a very large specific surface area due to colloidal size (Waychunas et al. 1994). More Fe-ox, as in the sediments from the Arcachon lagoon, would imply larger authigenic particles or thicker coatings on other particles and therefore fewer surface adsorption sites per unit weight or volume. In turn this would lead to higher Fe/P ratios, as observed. Other factors may also play a role, for example competition with As and OM for binding sites (e.g. Manning and Goldberg, 1996; Hunt et al., 2007).

The Mn-asc concentration in the Adour estuary sediments is close to the mean value of Mn-asc measured in particles from the turbidity maximum zone of the Gironde estuary that drains the same geological domain (Pyrenean belt). A similar mean value of  $8 \mu\text{mol g}^{-1}$  is also reported for the suspended particles of the nearby Bay of Biscay (Anschutz and Chaillou, 2009). On the contrary, the Mn-ox concentration of  $1.4 \mu\text{mol g}^{-1}$  found in the Arcachon lagoon surface sediment is very low but can be explained by the fact that the portion of sampled sediment consisted mostly of anoxic sediment. Actually, the thickness of the oxic layer of these sediment does not exceed 3 mm depth below the sediment water interface (Delgard et al., 2012), whereas we sampled a 3 cm thick sediment layer. Nevertheless, profiles of Mn-asc reported for Arcachon bay sediments indicate that the oxic layer does not contain more than  $2 \mu\text{mol g}^{-1}$  (Deborde et al., 2008a; Mouret et al., 2016). This low value is related to the nature of the soil of the watershed that is very poor in manganese. Therefore, one of the main difference between the Arcachon and Adour sediment is that the first is very

poor in Mn-ox, whereas the second contains a more typical concentration for the region, and thereafter we attempt to relate the different reaction pathways to the initial composition of each sediment.

#### 4.2. *Organic matter mineralization.*

The accumulation of dissolved inorganic nitrogen (DIN) during the experiments can be related to organic matter mineralization. The initial conditions were relatively comparable in the two slurries with high concentrations of ammonium but nitrate close to zero. Several experiments showed that for relatively refractory land-derived organic matter, aerobic respiration is almost always faster than anaerobic respiration (Aller, 1994, 1998; Kristensen et al., 1995; Andersen, 1996; Hulthe et al., 1998). During the lagoon sediment experiment, DIN accumulation occurred at a mean rate of  $23 \mu\text{M day}^{-1}$  but slightly higher rates were observed during the oxic period ( $44 \mu\text{M day}^{-1}$ ) suggesting that a labile fraction was involved in anaerobic respiration processes, and possibly an additional less labile one in the presence of dissolved oxygen. In the estuarine sediment experiment, DIN also accumulated during the first anoxic period but at a slower rate ( $12 \mu\text{M day}^{-1}$ ) compared to the same conditions in Arcachon sediments. Measurements of the lability of particulate organic matter have been performed for Arcachon Lagoon sediments (Relexans et al., 1992; Dubois et al., 2012), but not for the Adour estuary. Lower rate of DIN production is probably due to the higher proportion of less reactive continental organic matter in estuarine particles. During the oxic period, DIN concentrations did not increase significantly. The highest DIN rise occurred during the oxic-anoxic transition, suggesting that labile organic matter became suddenly available during this transition. The recycling of bacteria biomass accumulated during the oxic period that died because of the redox transition could be at the origin of this new DIN (Aller, 1998).

#### 4.3. Potential redox reactions during the experiments

Several reactions involving Mn, Fe, N, and P species may occur in these experiments and can explain our observations. Table 2 shows the common half-redox reactions of electron acceptor reduction and associated equilibrium constant for one electron transfer at standard conditions for major species involved during early diagenesis. The standard condition for concentration is 1 M, including  $H^+$ . The stoichiometry of these half reactions shows that the proton activity has a significant effect on  $\text{Log}K$  and the variation of  $\log K$  ( $\Delta\log K$ ) can be represented as a function of pH (e.g. Luther et al., 1997; Bethke et al., 2011) in order to get the equilibrium value at the pH of our incubations experiment. The pH was generally lower during oxic periods than during anoxic periods, but it remained at  $7.3\pm 0.4$ . The half reaction stoichiometry shows that the activity of N or S species does not influence markedly the equilibrium constant, because of the small values of the stoichiometric coefficient. However, the concentrations of Mn and Fe significantly influence the equilibrium of half reaction of Mn-ox and Fe-ox reduction. At standard conditions Mn-oxides or oxihydroxides cannot oxidize ammonium to nitrate, but as a concentration of  $Mn^{2+}$  of 100  $\mu\text{M}$  (rigorously, an activity of  $10^{-4}$ ) or less is considered, ammonium oxidation to nitrate by Mn(III) and Mn(IV) species gains the thermodynamic advantage (Fig. 3). It has been pointed out by several authors that the reduction of Mn-ox by diffusing ammonia could be an important process of di-nitrogen production (e.g. Hulth et al., 1999; Anschutz et al., 2000). Anaerobic nitrate production has been observed in several marine sediments (Aller et al., 1998; Anschutz et al., 1998; Mortimer et al., 2002; Deflandre et al., 2002; Chaillou et al., 2007), due to oxidation of ammonia by Mn(III)-oxyhydroxides (Hulth et al., 1999; Anschutz et al., 2005). Dissolved Mn(II) could theoretically be oxidized by nitrate to give  $N_2$ , as proposed in several studies (Aller, 1990; Schulz et al., 1994; Murray et al., 1995; Luther et al., 1997) and as shown by thermodynamic calculations (Fig. 3), but this reaction has not been directly observed in the



field (Thamdrup and Dalsgaard, 2000). Dissolved Mn(II) and nitrate generally co-exist below the oxygen penetration depth in sediment cores (Mouret et al., 2010), suggesting that the latter is not an efficient oxidant for the first.

Thermodynamic calculations show that nitrate is an oxidant for  $\text{Fe}^{2+}$  at both standard or corrected dissolved iron concentrations. The penetration depth of nitrate below the sediment-water interface generally fits with the upper boundary of dissolved  $\text{Fe}^{2+}$  detection (e.g., Hyacinthe et al., 2001, Mouret et al., 2016). Evidence for anaerobic reduction of nitrate to  $\text{N}_2$  with  $\text{Fe}^{2+}$  has been found in many field investigations (e.g. Hauck et al., 2001 ; Straub et al., 1996). Oxidation of Fe with  $\text{MnO}_2$  is a thermodynamically feasible process. This process has been proposed by several authors to explain the removal of  $\text{Fe}^{2+}$  and a part of the reductive dissolution of particulate Mn during early diagenesis (Myers and Nealson, 1988; Postma, 1985; Hyacinthe et al., 2001) or in stratified waters (Davison, 1993 ; Anschutz and Blanc, 1995 ; Crowe et al., 2008).

#### 4.4. Succession of reactions during the redox oscillations.

4.4.1. *Fe reactivity with oxygen, sulphur and nitrate.* The collapse of dissolved iron during the aeration periods suggests that dissolved Fe(II) was rapidly oxidized to a Fe(III) non soluble species. In the Arcachon experiment, an accidental oxygenation occurred between day 4 and day 7 and about  $420 \mu\text{mol L}^{-1}$  of iron precipitated. As the concentration of particles was  $93 \text{ g L}^{-1}$ , this new Fe(III) phase represented an addition of  $4.5 \mu\text{mol g}^{-1}$  of Fe-asc to the solid fraction. Given the analytical precision, this change was undetectable compared to the initial concentration of  $180 \mu\text{mol g}^{-1}$  of Fe-asc. However, this accidentally removed fraction was rapidly recovered once the conditions became anoxic again, since the concentration of dissolved iron reached  $417 \mu\text{M}$  on day 10. This suggests that the freshly precipitated Fe(III) phase, but not the initial Fe-asc fraction, was very reducible with a fast kinetic of reduction (Bonneville et al., 2004). The fast recovery of dissolved iron did not match with a

simultaneous increase in dissolved ammonium, which suggests that the electron donor for iron reduction was not in organic matter assuming that organic matter mineralization would have logically produced ammonium. The Fe(III) may have been reduced by FeS because even if dissolved sulphide was not detected, some FeS may have remained in the slurry after the oxidation accident, as the oxidation rate of this species with O<sub>2</sub> is about three orders of magnitude lower than the oxidation of Fe<sup>2+</sup> with O<sub>2</sub> (Millero et al., 1987; Wang and VanCappellen 1996). After several days of oxic conditions, dissolved Fe<sup>2+</sup> appeared again during the last anoxic cycle in the Arcachon lagoon slurry but its increase was slower than after the accidental oxidation event, which suggests that the rate of Fe(III) phase reduction depended on the time of exposure to dissolved oxygen. In the Adour sediment, the 40 µM of dissolved Fe<sup>2+</sup> dropped immediately to zero as conditions became oxic. However, because nitrate accumulated in pore waters, dissolved reduced iron could not be recovered when the conditions became again oxygen-free.

*4.4.2. P availability constrained by Fe.* Dissolved inorganic P collapsed down to zero in the Arcachon lagoon sediment during the first accidental oxidation event and did not reach its initial value, despite the reduction of Fe-ox when the conditions became anoxic again. On the contrary in the estuarine slurry, DIP did not drop to zero during the oxic period. The scavenging of P by Fe-ox is a well known process (e.g., Lijklema, 1980; Sundby et al., 1992). The molar ratio between oxidized Fe and scavenged P was much higher in the Arcachon slurry ( $423/10.7 = 39.5$ ) than in the Adour slurry ( $45/9 = 5$ ), indicating that the capacity of fresh Fe-ox to sequester P was much higher than available P in the Arcachon sediments. Therefore, P liberated from the reduction of a part of fresh Fe(III) and from organic matter mineralization was probably directly trapped on remaining Fe(III) phases. In the Adour slurry, newly formed adsorption site of precipitated Fe-ox were probably saturated with phosphate

because of the low Fe/P ratio. This most likely explains why DIP was not titrated during oxic periods.

*4.4.3. Mn reactivity constrained by oxygen and Fe.* Dissolved Mn concentrations decreased slowly during oxic periods, due to the slow kinetics of  $\text{Mn}^{2+}$  oxidation at the pH of the slurries (Morgan, 2000) even if the presence of Mn-ox catalyses the rate of Mn(II) oxidation (Davies and Morgan, 1989). Mn-ox content was very low in the Arcachon lagoon slurry, which may explain the very low decrease in dissolved Mn during the oxic period. Nevertheless, we observed a fast decrease at the beginning of this oxic period, when dissolved Fe collapsed, suggesting that the Fe(III) phase that precipitated trapped dissolved P, and probably a fraction of dissolved Mn too. Similarly, in subsurface anoxic sediments, the Mn(II) that is produced by reductive dissolution of manganese oxides can be in part adsorbed onto sediment particles and released to the porewater (Van der Zee *et al.*, 2001; Sundby, 2006). Adsorption occurs more rapidly than oxidation and allows a fraction of dissolved manganese to be trapped (Richard *et al.*, 2013). In the Adour sediments, dissolved Mn was quantitatively removed during the oxic period, and then it was partly recovered after the day 12. The initial high concentration of Mn-asc probably accelerated the rate of  $\text{Mn}^{2+}$  oxidation, which may explain the difference in  $\text{Mn}^{2+}$  decrease between both slurries.

In Arcachon sediments ammonium accumulated in waters during anoxic periods. It did not decrease during oxic conditions. Nitrate appeared after a few days of oxic conditions probably from particulate organic nitrogen oxidation, not from nitrification of ammonium, which seemed to be inhibited. Nitrate was reduced rapidly under anoxic conditions. The increase in the slope of ammonium concentration while nitrate decreased suggests that dissimilative reduction of nitrate to ammonium (DRNA) occurred. The slight decrease in DIN concentration between day 19 and day 20 also suggests that denitrification or anammox process occurred at the beginning of the second anoxic period. In the Adour estuary slurry

ammonia was quantitatively oxidized to nitrate in the presence of O<sub>2</sub>. Under anoxic conditions after day 10 nitrate remained in solution and even increased. This suggests that anoxic nitrification occurred. Thermodynamic calculation indicates that in absence of dissolved oxygen, anoxic nitrification only is possible in the presence of Mn-ox, which is the case for the Adour estuary slurry experiment. Javanaud et al. (2011) showed that the bacteria strain M4AY14 only expressed anaerobic nitrification when Mn-ox were present at ranges equal to or higher than those of nitrate. Nitrate is supposed to be ultimately denitrified, but denitrification was not complete in the Adour experiment, because it was most likely limited by labile organic matter availability.

#### 4.5. *Summary*

To recap, the differences in the succession of redox processes between the two incubation experiments was probably partly explained by the nature of organic matter as an electron donor, but it was also explained by the coupling between transition metal redox cycle and nutrient cycle. In one case water accumulated ammonium when Mn-ox was lacking and in the other case waters accumulated nitrate in the presence of Mn-ox. In Mn-ox depleted sediment, we can propose that there is no anaerobic oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>. The removal of NO<sub>3</sub><sup>-</sup> during suboxic periods allows dissolved Fe(II) accumulation. High dissolved Fe(II) accumulation during anoxic periods induces the titration of DIP when oxic events occurs. For the Mn-oxide enriched sediment oxidation of NH<sub>4</sub><sup>+</sup> occurs, but reduction of nitrate is inhibited. NO<sub>3</sub><sup>-</sup> present during suboxic periods promotes oxidation of dissolved Fe(II) coupled to NO<sub>3</sub><sup>-</sup> reduction, probably to N<sub>2</sub>. Therefore, dissolved Fe(II) content during anoxic periods remains at low level. When the redox state turns to oxic conditions, this small amount of Fe(II) is oxidized, but DIP is not entirely titrated because only few Fe-ox precipitates.

Marine sediments generally contain manganese oxides in the oxic layer and their advection to the suboxic zone is ubiquitous in the coastal zone, because bioturbation takes place across the redox boundary or the oxygen penetration depth oscillates daily or seasonally. It also occurs frequently in deep sea sediments (e.g. Gobeil et al., 1997). Several studies reported that the concentration of nitrate was not actually at zero below the layer of denitrification. Our investigation shows with an amplified experimental approach that anoxic nitrate production is linked to the presence of Mn-oxides. Because of this suboxic nitrate production, the oxidation of Fe(II) coupled to nitrate reduction occurs efficiently in the suboxic layer of a sediment and inorganic phosphorus is consequently trapped on authigenic Fe(III) particles. Sediments depleted in Mn-oxides are atypical, but can be found in some coastal environments like the Arcachon lagoon and sandy beach sediments. In such sediment, ammonium may accumulate preferentially in the oscillating or the bioturbated layer and dissolved iron can accumulate as well in the absence of oxygen as anaerobic nitrate production does not occur. DIP is not trapped under suboxic conditions but when shifted toward oxic conditions, such sediment then represents an effective trap of DIP powered by rapid and substantial Fe-ox authigenesis.

## **5. Conclusions**

Oscillating redox experiments allowed us to examine changes in water compositions that match with thermodynamic calculations. The Mn-N-Fe coupling outlined here, and deserving further investigations, is an apparent indirect oxidation of Fe(II) by Mn-ox through anaerobic nitrification (with Mn-ox) and denitrification (with Fe-ox). The presence or absence of reactive manganese oxide represents a major variable of the evolution of a redox oscillating sediment, because Mn-oxides intervene in the N cycle, which plays a part in the Fe cycle. The

redox Fe cycle ultimately determine the DIP availability. Therefore the initial content of Mn-oxide, or the input of new Mn-oxide in an oscillating environment may partly determine the speciation and the availability of nutrient in natural pore waters.

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Table 1.

Averages ( $\pm$ SD) of the biogeochemical parameters measured in the solid fraction of the Adour and the Arcachon sediments used for the incubations.

	Adour estuary slurry	Arcachon lagoon slurry
Organic carbon (dry weight %)	$3.2 \pm 0.1$	$4.2 \pm 0.1$
Mn-asc ( $\mu\text{mol g}^{-1}$ )	$9.8 \pm 1.0$	$1.4 \pm 0.2$
Fe-asc ( $\mu\text{mol g}^{-1}$ )	$47.0 \pm 5$	$180.0 \pm 20$
P-asc ( $\mu\text{mol g}^{-1}$ )	$9.8 \pm 1.5$	$11.0 \pm 2.0$

Table 2.

Half-redox reactions written with one electron transfer with the electron on the left side of the reaction and equilibrium constant ( $p\Box^\circ$  or  $\text{Log}K$ ) at standard state condition (1M in all species)

Half redox reaction	$p\Box^\circ$ ( $\text{Log}K$ )
$1/4 \text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow 1/4 \text{CH}_2\text{O} + 1/4 \text{H}_2\text{O}$	-0.20
$1/4 \text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow 1/2 \text{H}_2\text{O}$	20.78
$1/5 \text{NO}_3^- + 6/5 \text{H}^+ + \text{e}^- \rightarrow 1/10 \text{N}_2 + 3/5 \text{H}_2\text{O}$	21.03
$1/3 \text{NO}_2^- + 4/3 \text{H}^+ + \text{e}^- \rightarrow 1/6 \text{N}_2 + 2/3 \text{H}_2\text{O}$	25.54
$1/8 \text{NO}_3^- + 5/4 \text{H}^+ + \text{e}^- \rightarrow 1/8 \text{NH}_4^+ + 3/8 \text{H}_2\text{O}$	14.88
$1/2 \text{MnO}_2 + 2 \text{H}^+ + \text{e}^- \rightarrow 1/2 \text{Mn}^{2+} + \text{H}_2\text{O}$	20.78
$\text{MnO}(\text{OH}) + 3 \text{H}^+ + \text{e}^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O}$	25.34
$\text{Fe}(\text{OH})_3 + 3 \text{H}^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 3 \text{H}_2\text{O}$	18.28
$\text{FeO}(\text{OH}) + 3 \text{H}^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 2 \text{H}_2\text{O}$	13.60
$1/8 \text{SO}_4^{2-} + 5/4 \text{H}^+ + \text{e}^- \rightarrow 1/8 \text{H}_2\text{S} + 1/2 \text{H}_2\text{O}$	5.08
$1/8 \text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow 1/8 \text{CH}_4 + 1/4 \text{H}_2\text{O}$	2.86
$1/6 \text{N}_2 + 4/3 \text{H}^+ + \text{e}^- \rightarrow 1/3 \text{NH}_4^+$	4.64
$1/6 \text{NO}_2^- + 4/3 \text{H}^+ + \text{e}^- \rightarrow 1/6 \text{NH}_4^+ + 1/3 \text{H}_2\text{O}$	15.09
$1/2 \text{NO}_3^- + \text{H}^+ + \text{e}^- \rightarrow 1/2 \text{NO}_2^- + 1/2 \text{H}_2\text{O}$	14.27

$\text{Log}K$  derived from Robie et al. (1978) and Stumm and Morgan (1996)

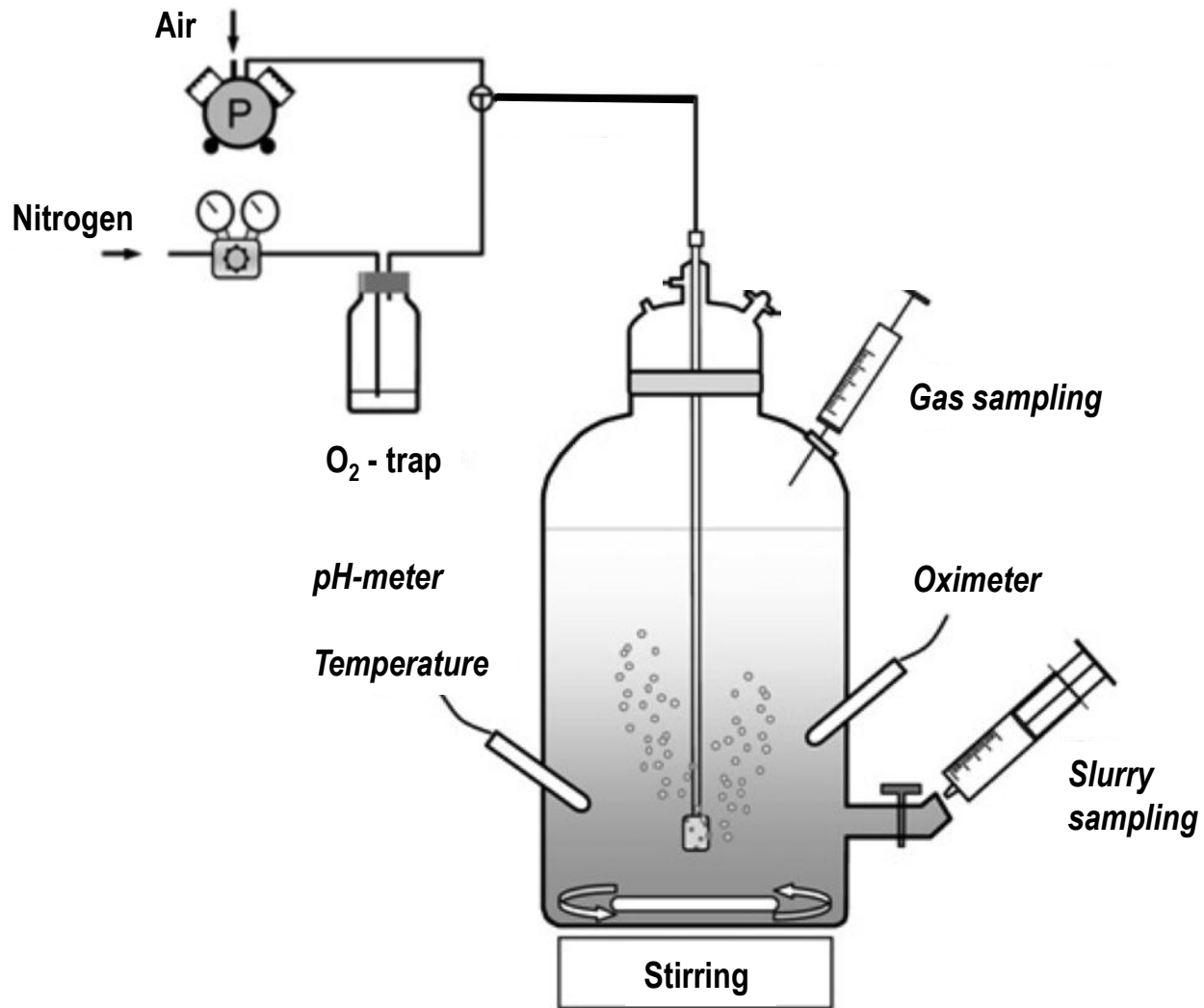


Figure caption

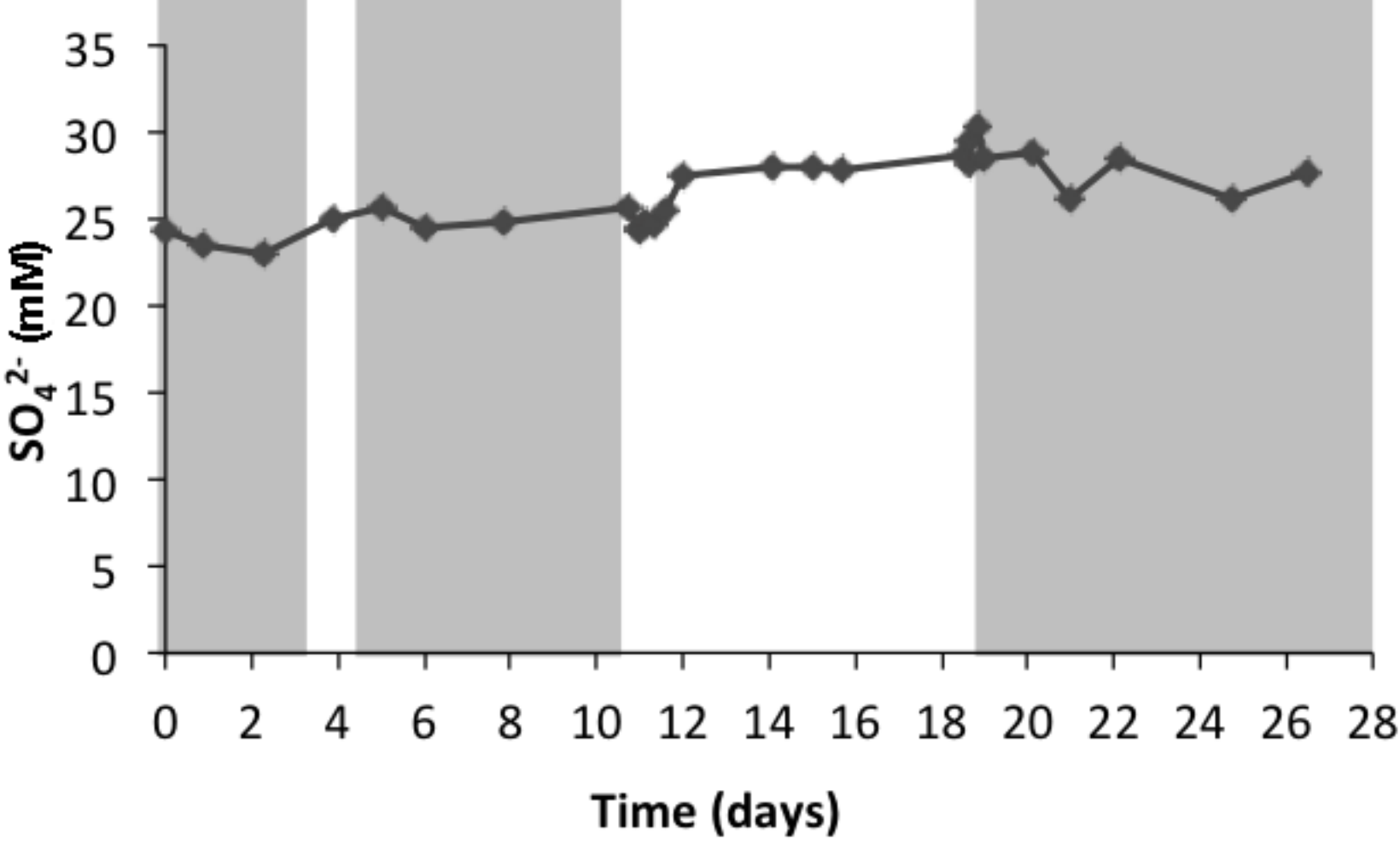
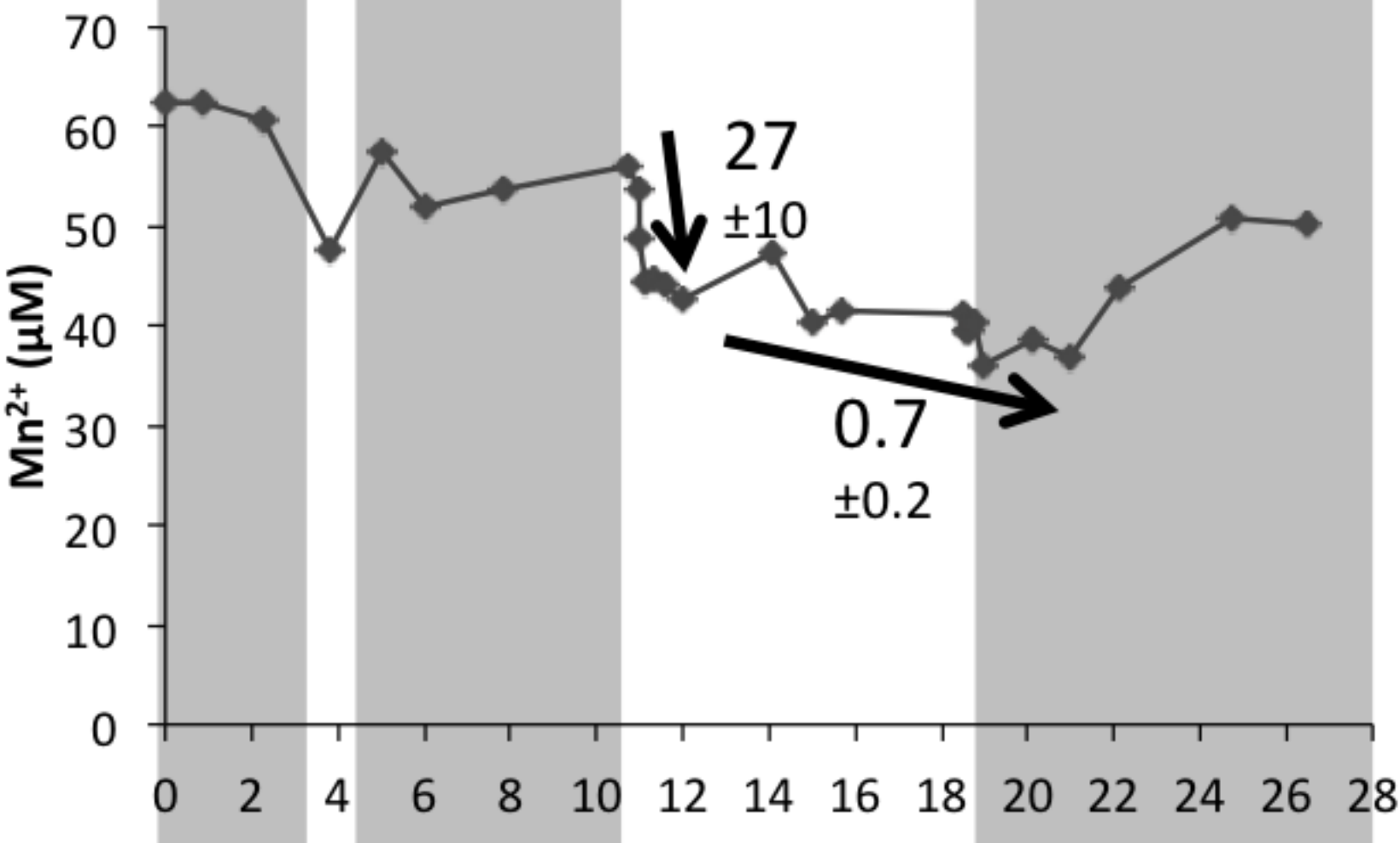
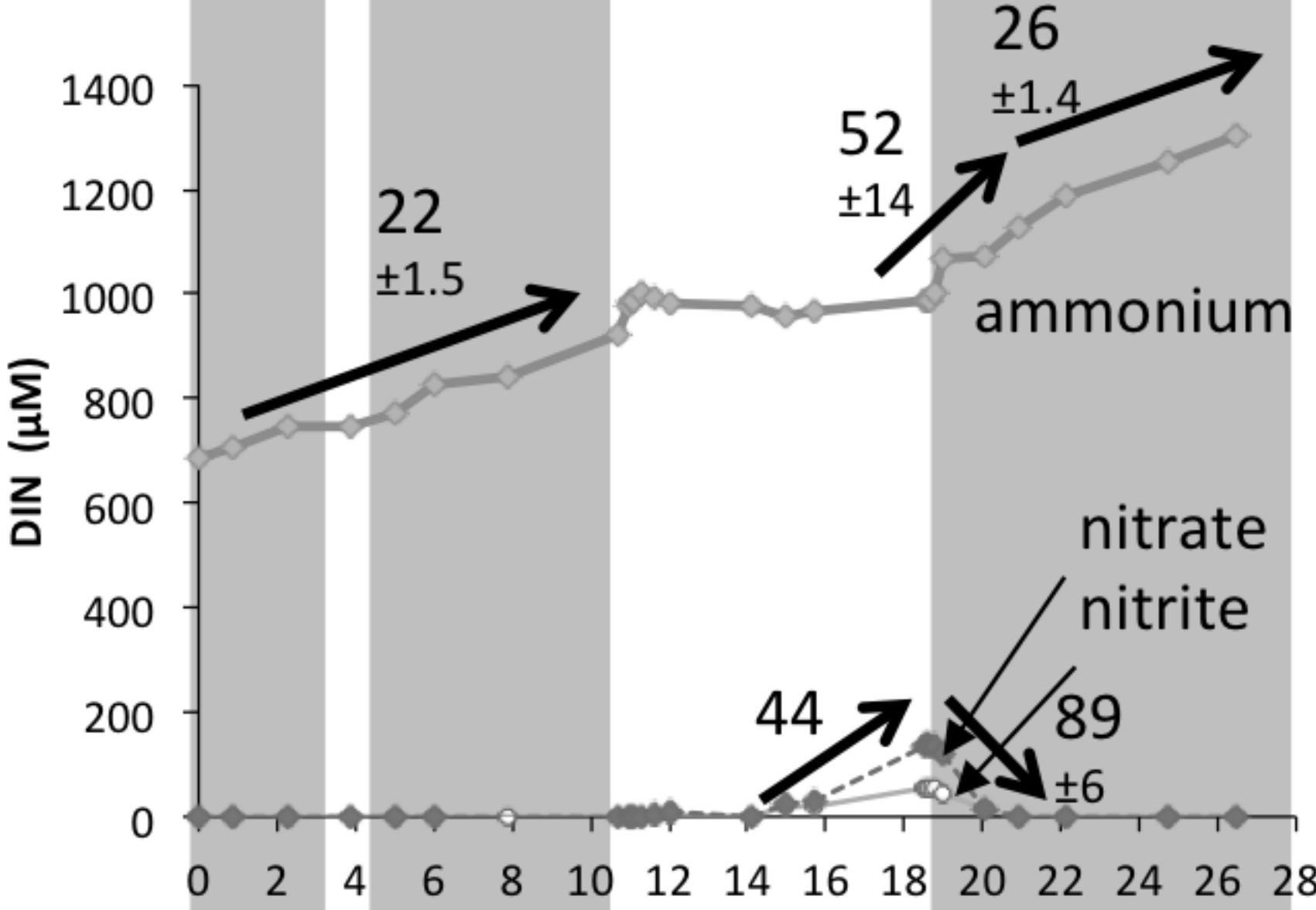
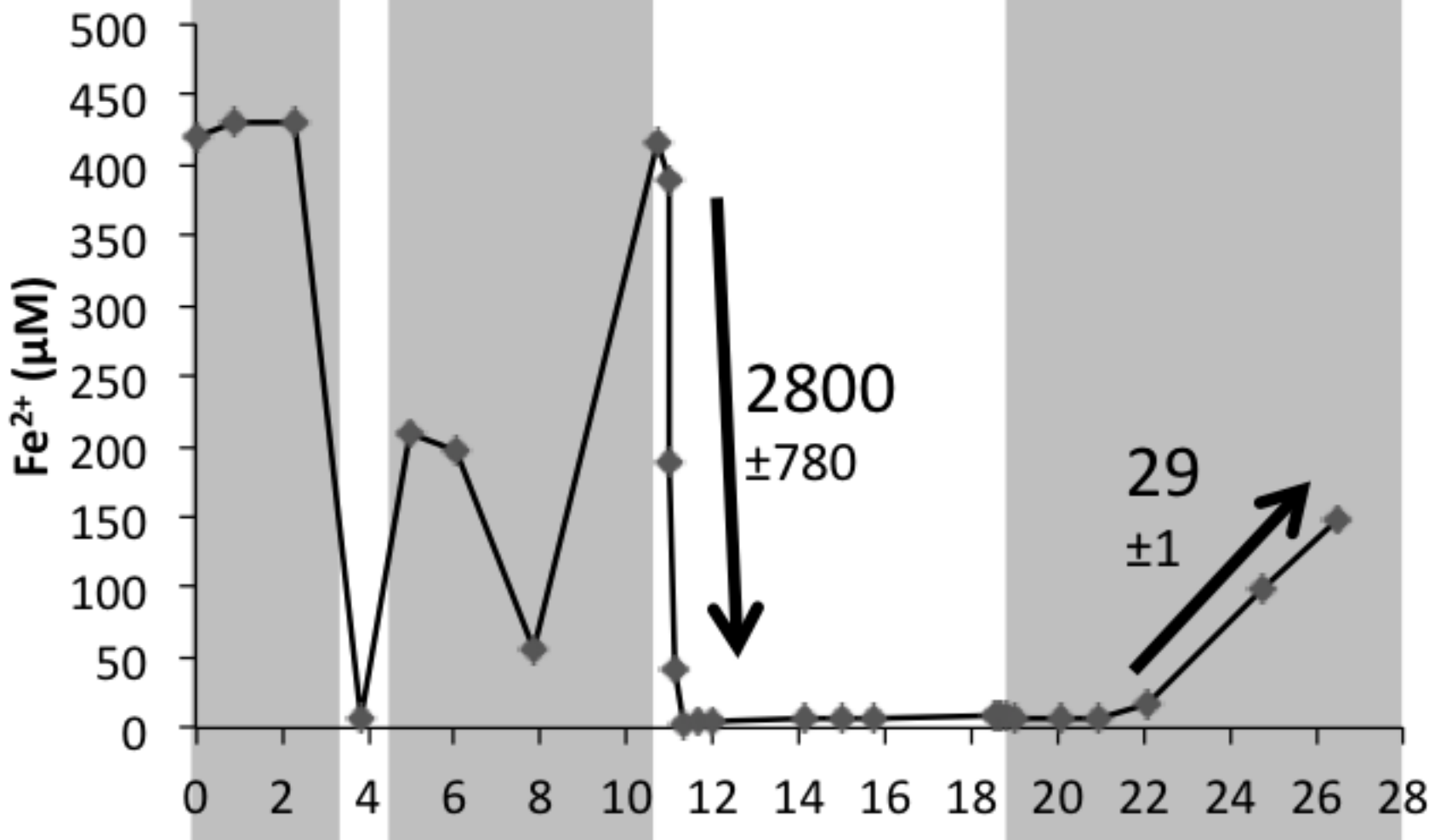
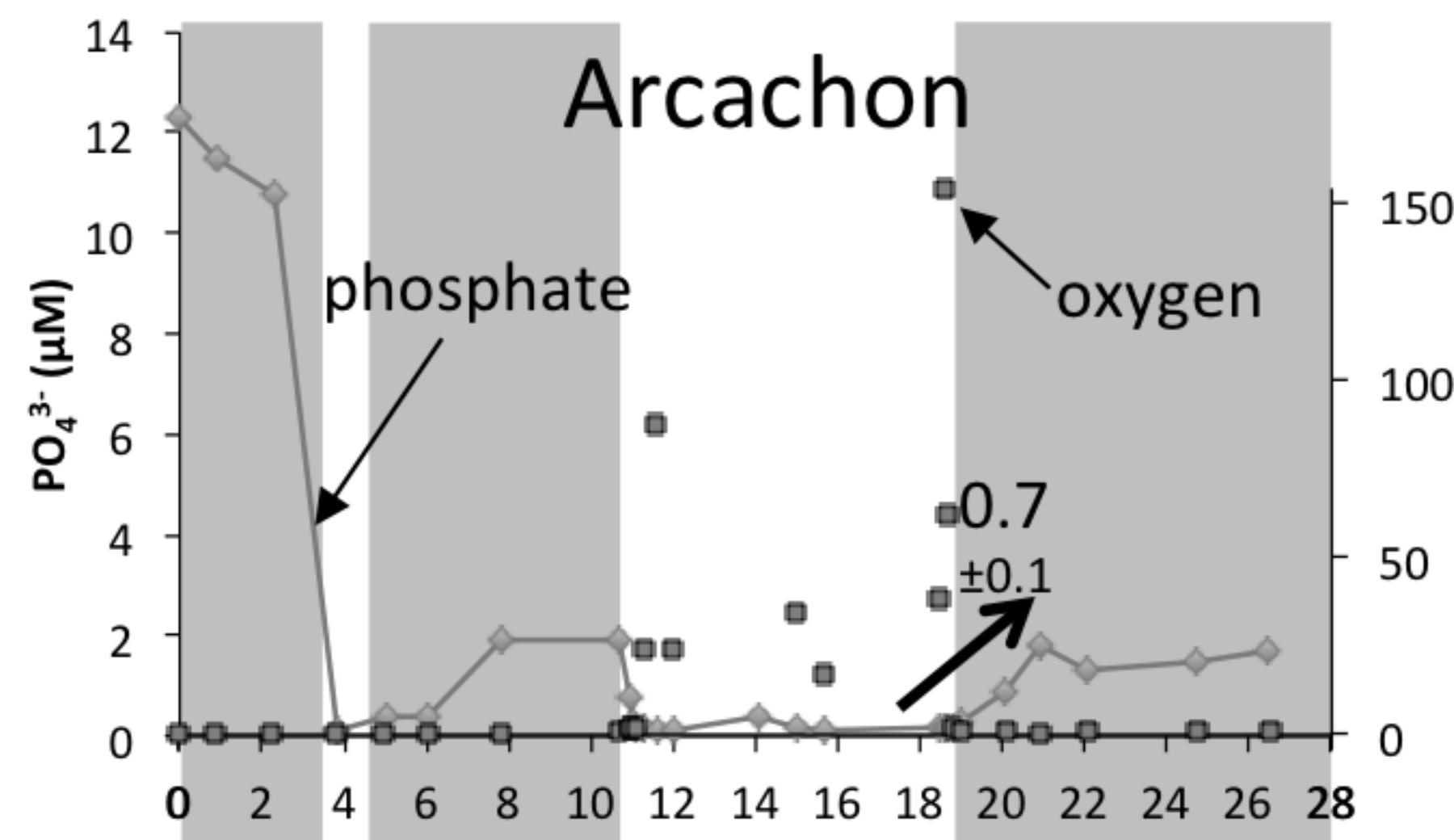
Figure 1 : Experimental set-up for incubation of the slurries in oxic or anoxic conditions.

Figure 2 : Evolution with time of concentration of redox-sensitive species in the Arcachon lagoon sediment slurry (left) and the Adour estuary sediment slurry (right). Grey areas represent anoxic period. Arrows show the rate of change in  $\mu\text{M day}^{-1}$ . Rates of reactions were determined using the slope of linear regression of concentration evolution with time. Error margin were calculated with the standard deviation of the slope.

Figure 3: Variation of  $\log K$  ( $\Delta\log K$ ) with pH and an activity of  $10^{-4}$  for  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  for selected half-reactions of Table 2. The grey area shows the range of pH during the redox oscillation experiments. All these reactions may be associated in pairs. The energy yield is favourable when the oxidant species of a redox reaction is that of the half reaction that has the highest  $\log K$ , and the electron donor species is that of the half reaction with the lowest  $\log K$ . The total free energy of pairs of half-redox is proportional to the vertical distance between the two lines ( $\Delta G^\circ_r = -\Delta(\Delta\log K) \times (RT \ln 10)$ )



# Arcachon



# Adour

