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Nutrient dynamics at the sediment-water interface in a Mediterranean lagoon (Thau, France): influence of biodeposition by shellfish farming activities

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Abstract

The Thau Lagoon, a French Mediterranean shallow lagoon, is the place of shellfish farming. The aim of the present work was to evaluate the role of this activity on nutrient exchange at the sediment-water interface in relation to organic matter (OM) sedimentation and degradation. Two stations inside (C5) and ouside (C4) the shellfish farming areas were sampled at 3 seasons. Porewater chemistry surveys and calculated diffusive fluxes were used to evaluate the trophic status of the Thau lagoon. Quantitative (Particulate Organic Carbon) as well as qualitative OM analysis (Hydrogen Index, Carbohydrates) were performed on sediments to assess OM characteristics. Results emphasized that surficial sediments at C5 are always more enriched in OM. Porewater nutrients concentrations are 10 to 20 times higher at C5 than at C4. In June 2003, the porewater profiles exhibit a sharp gradient at the bottom waters, indicating a hypereutrophic status, leading to an anoxic crisis.

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1. Introduction

The French Mediterranean coast is bordered by several shallow lagoons formed during the lastest 10 000 years at the favour of the lastest marine transgression. These lagoons, located in a rather densely populated transition zone between the continent and the sea, constitute very fragile ecosystems well adapted to study the impact of Man on the Environment. As a matter of fact, these lagoons, and especially Thau, suffer from eutrophication as a result of (i) excessive nutrient inputs from the catchment, (ii) very low water renewal (water residence time of about 3 months) and (iii) specific climate conditions (high temperature, limited rainfull periods, low tidal currents, Bacher *et al.* , 1996).

Thau, the biggest of the lagoons, is the site of shellfish farming. The shellfish production zones cover 1/5 of the lagoon area and its annual production represents about 15 000 t. The continual immersion of farming structures involves an abundant epibiose development on the oysters-mussels cords. The presence of these heterotrophic organisms (oysters and epibionts) in the water column modifies the transfer and the transformation of organic matter (OM) within the lagoon ecosystem (Mazouni *et al.*, 1996; 1998). For example, sedimentation fluxes have been estimated from 100 to 400 mg $C.m^2.h^{-1}$ in shellfish areas. These fluxes, 2 to 4 times higher than in the areas without shellfish, are susceptible to increase the sedimentation rate (Grenz *et al.* 1992). In addition, the combination of high OM productivity, high summer temperature (25°C water surface temperature), low wind speed, induces the rapid depletion of dissolved oxygen and subsequent anoxia (Harzallah & Chapelle, 2002). Anoxic conditions develop in summer both at the sediment-water interface and at the bottom of the water column. These anoxic episodes, locally named “malaigues”, induce a high turbidity and H_2S smell during the summer months with a large shellfish mortality.

Previous studies have established that the sediment compartment is a sink for particulate phosphate (Boström *et al.*, 1982, 1988; Caraco *et al.*, 1990). This compartment could also become a source through the release of dissolved species under well defined pH and Redox conditions (Boers, 1991; Song & Müller, 1999). Numerous parameters influence the exchange of nutrients at the sediment-water interface and emphasize the influence of multi-environmental parameters such as bacterial activity (Gächter & Meyer, 1993), iron-hydroxide chemistry or oxygen conditions (Maine *et al.,* 1992; De Montigny *et al.* 1993). Moreover, OM buried in sediments may impact the nutrient release by forming refractory organo-metallic complexes with iron and phosphorus (Paludan and Jensen, 1995; De Groot and Golterman, 1993; Hirata, 1985). Even if these complexes are subjected to microbiological mineralisation as a carbon and an energy source, their low availability may delay the nutrient release. If this low bioavailable OM quantity exceeds the bacterial mineralisation capacity of the sediment, these complexes will accumulate in the sediment compartment as a ‘residual organic phosphate‘ fraction (De Groot and Golterman, 1993) that will only be remobilised with difficulty. The sedimentary OM content is not sufficient to discuss the nutrients release at the sediment-water interface, measurements of OM quality and degradation rate being needed to access to the extent of degradation of sediment organic components.

The aim of the present work is to discuss the role of shellfish farming on the nutrient exchange dynamic at the sediment-water interface in two contrasted sites of the Thau Lagoon : inside and ouside the shellfish farming areas. A seasonal porewater survey was investigated at these two sites in Winter 2001-02, Spring 2002 and Summer 2003, reflecting contrasted trophic levels in the lagoon. As little is known on Thau sediment OM, this study is focussed on OM characterisation from the quantitative (Particulate Organic Carbon) as well as the qualitative (Hydrogen Index, Carbohydrates) point of view. The interpretation of OM degradation rate should allow take into account the influence of shellfish biodeposits on the exchange of nutrient at the sediment-water interface.

2. Material and methods

2.1 Site

The ‘Thau’ Lagoon, a Mediterranean shallow coastal lagoon is located in the South of France (3°32’ to 3°42’E and 43°20’ to 43°28’N). Its total surface is about 75 km^2 with a length of 19.5 km and a width of 4.5 km. Its depth varies from 4 to 10 meters. At each extremities, the lagoon is connected to the sea inducing a water residence time of about 3 months.

Two different sampling stations were chosen in contrasted areas of the shallow lagoon: the first site (station C4) was located in the middle of the lagoon (N43°24.018, E3°36.703; average depth: 8 m.) and the second site (station C5) inside of the oyster bank zone A, adjacent of Bouzigues (figure 1; N43°25.994, E3°39.657; average depth: 8.5 m.).

Fieldtrips were carried out, at the two sampling stations, at three different times of year, namely in (i) Winter 2001-02 (05/12/01 to 09/12/01; insertion of diffusion samplers to be removed in January 2002 after 3 weeks equilibration), (ii) Spring 2002 (15/04/02 to 21/04/02; insertion of diffusion samplers in March 02, removal in the 18/04/02 after 3 weeks equilibration), (iii) Summer 2003 (19/05/03 to 23/05/03; insertion of diffusion samplers to be removed the 26/06/03 after one month equilibration).

2.2 Sediment characteristics

The two sampling sites present a grey silty clayey sediment containing shells without physical structures. The sediment is mainly constituted by fine silt (10 to 20 µm). The mixed layer, at the C4 site, is restricted to the upper 3 cm. In contrast, the C5 site has a mixed layer of 10 cm depth (Schmidt *et al.* accepted, 2005). Composition of sediments has given the following composition: CaO=18.4%, MgO=1.97%, K_2O=1.71%, Na_2O=3.72%, Fe_2O_3=2.02%, Al_2O_3=8.54% (Péna & Picot, 1991). At the C4 site, the porosity is constant with depth with a value around 0.85. In contrast, the porosity of C5 site decreases from 0.90 at the sediment surface to 0.75 at 35 cm depth (Metzger *et al.* accepted, 2005). At the sediment surface to 40 cm depth, pH values vary from 8 to 8.4 at the C4 site and 7.4 to 8 at the C5 site (Metzger *et al.* accepted, 2005). The redox potential (Eh) in the sediment surface is about 200 mV whatever the site and the season whereas the redox measured in the first 10 cm of sediment showed significant seasonal variation. The redox values decrease during the year: Eh = 125 mV in winter and Eh = -50 mV in summer.

2.3 Sampling techniques

The pore water sampling was performed using diffusion samplers (Hesslein, 1976), with an inert polysulfone membrane of 0.2 µm porosity (Millipore, Durapore). The diffusion sampler design employed consists of a 51.5 $*$ 22 $*$ 3 cm Plexiglas sheet in which fixed volume (5.6 cm^3) chambers are spaced at 1 cm. Each diffusion sampler has two series of 40 chambers. In order to avoid oxygen contamination in the chambers, the diffusion samplers were bubbled with nitrogen in deionised water bath before their insertion. At the C5 and C4 sites at each sampling period, two diffusion samplers were inserted in the sediments, by scuba-divers, in an area of 2 m^2, leaving 6 or 7 chambers above the sediment surface and 33 or 34 below. The equilibration time required for the diffusion sampler is 3 weeks according to Bally *et al.* (2005). Pore water samples were removed using plastic syringes, in a glove box filled with nitrogen to prevent the co-precipitation of phosphate with iron-hydroxide. The samples acidified with 1N HCl and stored in conditionned 5 ml haemolysis tubes were frozen until analysed for phosphate (SRP), ammonia (NH_4^+) and Dissolved Organic Carbon (DOC) determination.

Sediment cores (Φ = 12 cm and length = 25 cm) were sampled by scuba-divers with Plexiglas® corers, at the C4 and C5 stations, in April 2002. Coring operations were carried out very carefully in order to prevent any disturbance of the top sediment where the water content is very high (96 % at the sediment surface; 86 % at 20 cm depth). Immediately after the sampling, the top 2 cm were cut into slices of 1 cm, except for the 2 first cm which was cut into slices of 0.5 cm (0-0.5 cm/ 0.5-1cm/ 1-1.5 cm/ 1.5-2 cm/2- 3 cm /3-4 cm/4-5cm/ …../19-20 cm for C4 and until 21-22 cm for C5). The sediment cakes obtained were stored in plastic bags filled with nitrogen and immediately frozen.

2.4 Sediment analysis

Rock-Eval pyrolysis (Espitalié *et al.*, 1985) was used for global organic matter quantititive and qualitative characterisation. Two main parameters may be provided by this technique : Total Organic Carbon (here named Particulate Organic Carbon "POC") and the Hydrogen Index (HI) which depends on the hydrogen OM content and the corresponding C/H (Espitalié *et al.*, 1985). The POC and the HI are expressed in % Organic Carbon weight and mg of Hydrocarbons per g POC (or mg HC .g^{-1} POC), respectively.

Rock-Eval® pyrolysis has been performed with an RE6 device of Vinci Technologies™. The analysis were carried out on 100 mg of crushed samples with a temperature of 200° C (20 min) up to 600° C at 25° C min^{-1} under a N_2 flow, followed by oxidation at 600° C for 7 min under an oxygen flow. All the analysis were performed in duplicate. Reproducibility determined after 68 analysis with the IFP 55000 reference material was +/- 2 % for POC content and +/- 6 % for HI (Disnar *et al.* 2003).

Carbohydrate analyses were performed on the top (0-2 cm) and the base (13-22 cm in C5 core and 10-20 cm in C4 core) in order to characterize the availability of carbohydrate at the sediment-water interface in contrast with deeper sediment. The procedure used for carbohydrate analysis derives from previous works (Bethge *et al.* , 1966; Oades *et al.*, 1970; Modzeleski & Laurie, 1971; Cowie & Hedges, 1984a). Briefly after hydrolysis (100°C; 3h.) with 0.5 M H_2SO_4 and cooling, an internal standard (6-deoxy-D-glucose; Wicks *et al.*, 1991) is added to the hydrolysate. The anomeric carbohydrate mixture is equilibrated with lithium perchlorate (0.2 %) in pyridine (Bethge *et al.*, 1966) and silylated with N,O-Bis(trimethylsilyl)trifluoroacetamide. Finally, the silylated carbohydrates were analysed on a Perkin-Elmer™ Auto System XL gas chromatograph. Peaks were identified through retention times and quantified using a standard mixture of eight neutral monosaccharides, namely, arabinose, rhamnose, ribose, fucose, xylose, mannose, galactose and glucose. Quantification was based on one of the major and better-resolved anomer peaks given by each studied compound (Bethge *et al.*, 1966). Total carbohydrates contents were calculated as the sum of the compounds identified and quantified. Analytical errors varied between 2.6 and 13 % depending on the type and the abundance of the compound considered (Ogier *et al.*, 2001).

2.5 Dissolved component analysis

Phosphate (SRP) and ammonia (NH_4^+) were measured using a colorimetric method (Stainton *et al.*, 1977) with a Bran+Luebbe™ auto-analyser Continuous Flow Analysis, according to the methods of Treguer & Le Corre (1975). The detection limits are 0.014 mg l^{-1} and 0.01 mg l^{-1} for phosphate and ammonia, respectively. DOC was analysed with a Shimatzu 5050™ TOC analyser with a detection limit of 1 mg l^{-1}. Measurements precisions are 5% RSD determined from repeated measurements (5 times) of the same sample and standard samples (Bally *et al.*, 2004).

2.6 Method for calculating Nutrient diffusive fluxes

The calculated diffusive fluxes were calculated using the first Fick's law adapted for sediments (I):

$$\mathrm{Js}=-D_s \times \frac{dC_i}{dx} \quad \text{(I)}$$

Js : Calculated diffusive flux ($\mathrm{mmol.m^{-2}.d^{-1}}$)

φ : Sediment porosity (dimensionless)

D_s : Diffusion coefficient of the species in sediment ($\mathrm{m^2.d^{-1}}$)

$\frac{dC_i}{dx}$: Profile gradient ($\mathrm{mmol.m^{-4}}$)

The diffusion coefficient in water ($D_w^0(X)$) was corrected from the Stockes-Einstein formula (II & III) given in Li & Gregory (1976):

$$D_w^0(NH_4^+)=19.8+0.4(T-25) \quad \text{(II)}$$

$$D_w^0(PO_4^{3-})=7.36+0.16(T-25) \quad \text{(III)}$$

with

$D_w^0(PO_4^{3-})$, Diffusion coefficient in water for PO_4^{3-} ($\mathrm{m^2.d^{-1}}$)

$D_w^0(NH_4^+)$, Diffusion coefficient in water for NH_4^+ ($\mathrm{m^2.d^{-1}}$)

T, sediment temperature (°C)

The diffusion coefficient in sediment is calculated from the formula (IV)

$$D_s(X)=\frac{D_w^0(X)}{\theta^2} \quad \text{(IV)}$$

θ^2 is the tortuosity obtained from the formula V (Boudreau, 1996)

$$\theta^2=1-2\ln\varphi \quad \text{(V)}$$

The porosity and the temperature used in flux calculation are reported in table 1.

3. Results

3.1 Bulk organic matter characterization (POC and HI)

At C5, Particulate Organic Carbon (POC) contents decreases sharply from 4.4 % at the top of the core to 3.3 % at 1.75 cm depth. This decreasing trend continues smoothly down to 8 cm depth to reach a value of 1.7 %. Below this depth, POC contents remain rather constant around 2% down to the base of the core (Fig. 5a, Table 3a). The Hydrogen Index HI values (hydrocarbon mg per g of Organic Carbon), remain constant with values around 370 mg HC g^{-1} POC in the upper 5 cm of the core. Below this depth, HI values first decrease downward to reach a value of 323 mg HC g^{-1} POC at 8 cm depth (Fig. 6a), then fluctuate between 217 and 335 mg HC g^{-1} POC (Table 3a).

At C4, POC contents increase slightly from 3 % at the top of the core to 3.2 % at 2 cm depth. Between 2 cm to 8 cm POC decreases with depth to reach a value of ca. 2.6 % at 8 cm depth and below this depth values remain constant down to 11 cm depth. Below 11 cm, POC contents vary between 2.8 to 4.2 % (Figure 5b, Table 3b). Hydrogen Index (HI) values decrease downcore from 354 mg HC g^{-1} g POC at the sediment water interface to 303 mg HC g^{-1} g POC at the base of the core (20 cm depth) (Table 3b).

3.2 Carbohydrate analysis

At C5, the total neutral carbohydrate concentrations decrease sharply with depth with a value of 3.6 mg g^{-1} (dry weight) near the sediment surface, 3.2 mg g^{-1} at 2 cm depth and only 1.3 mg g^{-1} at 22 cm depth (Table 3a). These compound concentrations indicate that carbohydrates contribute only to 7 to 12 % of POC. In the surficial sediments (0-2 cm) individual neutral carbohydrates are dominated by rhamnose (24 %) and fucose (21 %), followed by glucose (15 %), galactose (12 %), xylose (11 %), arabinose (9 %) and mannose (8 %) (Fig. 6a; Table 3a). Ribose which was often below the detection limit is thus not discussed further. At the base of the core (13-22 cm), neutral carbohydrates are dominated by fucose (24 %) and rhamnose (18 %), followed by glucose (14 %), arabinose (14 %), xylose (12 %), mannose (9 %) and galactose (9 %) (Fig.6c).

At C4, the total neutral carbohydrate concentration presents a rather high top core (0-2 cm) value of 2.5 mg g^{-1}. At 10 cm depth, carbohydrate concentrations are only 1.8 mg g^{-1}. Below this depth values increase slighly with large variations between 2.1 and 3.2 mg g^{-1} (Table 3b). These compound concentrations indicate that carbohydrates account for 5.4 % to 10.7 % of the POC. In the surficial sediment (0-2 cm) the weight percentages of individual neutral carbohydrates are dominated by glucose (23 %) and fucose (22 %), followed by xylose (13 %), galactose (13 %), arabinose (11 %), mannose (10 %) and rhamnose (8 %) (Fig. 6b Table 3b). Ribose is present at low concentrations and often below the detection limit. At the base of the core (10-20 cm), the weight percentages of individual neutral carbohydrates in sediments are dominated by glucose (20 %), fucose (19 %) and rhamnose (17 %), followed by xylose (15 %), galactose (14 %), mannose (9 %) and arabinose (8 %) (Fig. 6d).

3.3 Nutrient porewater profiles

Soluble Reactive Phosphorus (SRP)

At the C5 sampling station, in the bottom waters (up to 7 cm above the sediment-water interface), Soluble Reactive Phosphorus (SRP) concentrations were at the lowest in Winter (January 2001, Fig. 2a), and Spring (April, 2002, Fig. 2b) and then varied between 0.1 and 4 µM. In contrast, in Summer (June 2003, Fig. 2c), at the same site, SRP concentrations reached very high levels in the bottom waters: 20 µM at 10 cm over the water-sediment interface, up to 60 µM 5 cm below and finally 10 times higher values (600 µM) at the sediment interface. Always in summer, SRP concentrations decreased slowly below the sediment surface to reach 100 µM at 5 cm depth.

At the C4 sampling station, SRP concentrations reached about 1 µM in the bottom waters. However, these concentrations showed no change with depth. Moreover, no SRP concentration gradient was observed in the sediment at this site throughout the year.

Ammonia concentrations (NH_4^+)

At the C5 sampling station, ammonia concentrations (NH_4^+) fluctuated between 15 to 30 µM in Winter (Fig. 3a) and Spring (Fig. 3b) in the bottom waters. In contrast, in Summer (June 2003, Fig. 3c) they increased sharply, up to values of 500 µM, i.e. about 10 times more than during the previous sampling periods.

NH_4^+ profiles are also quite similar to those obtained for the other dissolved species (i.e. SRP and DOC). Again all nutrients gave similar profiles namely with a gradient between –5 and –15 cm, except for the Summer period (June 2003), where the concentration gradient was located in the bottom waters. The concentrations reached values of about 8000 µM at the sediment-water interface. Thus a concentration gradient is present in the bottom waters, but not in the sediment under the interface.

The porewater chemistry at the C4 sampling station is really different. At this site concentrations levels were low (< 50 µM) and these was no concentration gradients, the profiles being vertical (Fig. 3d, 3e).

Dissolved Organic Carbon (DOC)

At the C5 site the bottom waters (5 cm above the sediment-water interface) showed Dissolved Organic Carbon (DOC) contents increased sharply in Summer (June 2003, Fig. 4c) to reach values up to 10 000 µM. Then, DOC concentrations in the bottom waters were about 20 times higher than in Spring and Winter. In addition, a concentration gradient is observed in the bottom waters but not in the sediment as usually expected.

During Winter and Spring at C5, DOC concentrations increased continuously with depth in the sediments, to delineate a gradient down to 15 cm below the sediment-water interface. Below, DOC concentrations remained constant, in Spring, with values around 2000 µM. The variations of DOC concentrations with depth were better marked in Spring than in Winter. Because at this later season, results exhibit values from 1500 to 6000 µM (-15 cm depth). It is worth underling that whatever the nutrients considered, it delineates profiles comparable to those of DOC, namely with a steep gradient between 5 and 15 cm depth.

In Summer (June 2003, Fig. 4c), the sharp DOC concentration gradient which was observed in the bottom waters, was not accompanied by any marked concentration change with depth in the sediment where DOC levels raised up to 20 000 µM of Carbon.

At the C4 sampling station, DOC profiles showed the same shape than those already described for SRP i.e. without any change all over the 30 cm of water and sediment investigated. DOC concentrations reached about 500 µM in the bottom water and in the sediment in Winter and Spring (Fig. 4 d,e).

3.4 Diffusive nutrients fluxes

Fluxes have been calculated from concentration gradients observed for the nutrients profiles (Figs 2, 3 and 4). During Winter and Spring, these gradients were located between 5 and 15 cm below the sediment-water interface. At C5 station, calculated flux values fluctuated from 0.62 to 1.0 mmol.m^{-2}.d^{-1} NH_4^+ and from 0.3 to 0.14 mmol.m^{-2}.d^{-1} PO4 for Winter and Spring, respectively (Table 2). In contrast, at C4, the calculated fluxes values fluctuated from 0.2 to 0.05 mmol.m^{-2}.d^{-1} NH_4^+ and from 0.03 to 0.02 mmol.m^{-2}.d^{-1} SRP, for Winter and Spring, respectively (Table 2). Whatever the season, a spatial variation is evident, with fluxes about 10 times higher at C5 than at C4.

In Summer (June 2003) at C5 site, concentration gradients were not located below the sediment water interface (- 5 cm depth), but in the bottom waters (Figs 2c and 3c). High NH_4^+ and SRP flux values have been derived from these concentration gradients in the bottom waters (10,7 mmol.m^{-2}.d^{-1} and 0.96 mmol.m^{-2}.d^{-1} or respectively for NH_4^+ and SRP) (Table 2).

4. Discussion -

4.1 Nutrients profile, a tool to assess ecosystem trophic levels

As generally observed in mediterranean shallow coastal lagoons, the phosphate inputs originated from urban and agricultural effluents. In the Thau lagoon, these inputs have decreased by a half from 1971 to 1996 as a result of an improvement in wastewater treatment on the Thau catchment-coastal lagoon system (La Jeunesse & Elliot 2004). Over 30 years monitoring of water-column chemistry highlighted the decrease of phosphate concentrations. In the Seventies, the average phosphate concentration was 6 µM, increasing to 10 µM during anoxic summer periods. In contrast, the average phosphate concentration, actually measured in the water column, fluctuated from 0.04 to 1.2 µM. The decrease of 90% of annual mean phosphate concentration in the water column from 1971 to 1994 (Souchu *et al.* 1998) can be explained by the reduction of domestical effluents but also but the changes in land-use by an exceptional decrease of vineyards areas (La Jeunesse *et al.* 2002). On the other side, phytoplanctonic biomass is present in higher concentrations in the lagoon than in sea water, with an average chlorophyll a of 2 µg/l with maxima of 5 µg/l in summer periods. This primary production depicts a relatively high trophic level in the lagoon. During summer, OM degradation and nutrient release at the sediment-water interface trigger a high phytoplanctonic activity in the water column, particularly in shellfish areas (Casellas *et al.* 1990; Plus *et al.* 2001).

The knowledge of porewater chemistry is a prerequisite for assessing nutrient dynamic at the sediment-water interface. The presence of significant amounts of OM buried in the sediments is probably the main factor influencing nutrients fluxes at the sediment-water. As a matter of fact, the shape of nutrient profiles reflects the presence of organic matter (OM) layers undergoing mineralisation and thus acting as a source of dissolved nutrients as C, N and P. In coastal shallow lagoons, OM inputs originate mainly from land, in the form of plant residues, or in situ, in the form of “normal” phytoplankton production plus shellfish biodeposits. Indeed, the nutrient profiles led us to follow OM mineralization over depth. At the C5 station the sediments are anoxic. As a matter of fact, the depth of oxygen penetration is, at a maximum, limited to 5 mm in winter and 0.5 mm in summer (Dedieu *et al.* accepted 2005). This anoxic sedimentary environment entails anaerobic OM degradation, with oxidation reactions successively driven by the reduction of Mn and Fe oxides, then of sulphates and finally by methane fermentation processes (Song & Müller, 1999). All these processes are known to release monomeric low molecular weight compounds such as organic acids which may acidify the porewaters (Burdige & Gardner, 1998). The measurements of porewater redox-sensitive species at the C5 station (Metzger *et al.* accepted 2005) confirm the establishment of such anaerobic OM degradation. Another consequence of this process is the greater acidity of the sediment at C5 station than at C4 station over the upper 40 cm (Metzger *et al.* accepted, 2005). Moreover, these observations are consistent with the presence of more labile OM at the C5 station than at C4.

Discussion on the trophic level of aquatic ecosystems is often approached using porewater gradients. In oligotrophic ecosystems, the nutrient profiles are vertical, i.e. the concentrations remain at the same level throughout the water column and the sediment. In contrast, in eutrophic ecosystems nutrients profiles exhibit sharp gradients near the sediment-water interface. At C4 station, especially in winter, nutrients profiles exhibit a vertical shape, reflecting low biological activity consequentive to low input of biodegradable OM. In contrast, at the C5 station, nutrient profiles delineate high gradients in summer. The nutrient concentration increased down to 10 cm below the sediment-water interface (Figs 2c, 3c, 4c). Above, the nutrient profiles are vertical, with the same concentration levels in the water column than in the sediment. One hypothesis for this vertical profile is the homogeneisation of the sediment, explained by the 10 cm upper mixed layer in relation to rather high biological activity at the C5 station (Schmidt *et al.* accepted 2005)

Previous works on porewater nutrient chemistry, in the Thau laggon (Mesnage, 1994, Mesnage & Picot, 1995, Meztger *et al.* accepted, 2005), have demonstrated that nutrient concentrations (SRP and Ammonia) were three times higher inside the oyster banks than outside. Moreover, a sharp concentration gradient that appears below the sediment-water interface (-2 cm) evidences nutrient accumulation in porewaters (Mesnage, 1994). The impact of oysters on phosphate accumulation in surface sediments under the influence of their pseudo-faeces was also demonstrated: sediments inside of shellfish bank zone (zone B, Fig. 1) were more loaded in particulate phosphorus than those outside of the shellfish farming zone (Chapelle *et al.* 1994).

In contrast, with these previous works (Mesnage & Picot, 1995; Metzger *et al.* Accepted 2005), the most relevant fact in the present study, is the shape of nutrient porewater profiles measured in summer 2003. Indeed, these profiles have a very uncommun shape exhibiting a transient consequence of this shellfish impacted ecosystem. The concentration gradient is not limited to the 10 first cm below the water-sediment interface, instead, it extends above the sediment-water interface, at the base of the water column. This kind of profile (Figures 2a, 3a and 4a) is very close to the theorical one, described by Enell & Löfgren (1988), for shallow eutrophic lagoons exposed to high organic matter inputs (fish farming, phytoplankton or macro-algae sedimentation following the spring bloom). Thus, geochemical porewater results at C5, indicate a great seasonal variation evidenced by important increase of nutrients concentrations from Winter to Summer and provide a useful tool to evaluate the aquatic ecosytems trophic level, the difference between Summer and Winter nutrients concentrations being more pronounced in eutrophic ecosystems.

4.2 Organic matter buried in sediments, influence on nutrient release

The specific shape of nutrients porewater profiles in Summer 2003 is also supported by the data obtained on organic matter buried in the sediments. Indeed, POC values (3 to 4 % in the surficial sediments), are in the range of those found in carbon-rich aquatic ecosystems especially in other impacted lagoons (Crawford *et al.*, 2003). Such high values suggest a very probable contribution of shellfish feces to the OM buried in sediments. As a matter of fact, According to the literature, Mediterranean surficial sediments present POC contents lower than 1 % : 0.7 to 0.9 % in Gulf of Lions (Accornero *et al.*, 2003), 0.3 to 0.82 % in Cretan sea (Gogou & Stephanov, 2004). Others shallow lagoons in the world also present POC values in the same 0.1 - 2.8 % range (Rigollet *et al.*, 2004; Paez-Osuna *et al.*, 1998). When, surficial lagoons sediments present higher POC values (i.e. $3 < \mathrm{POC} < 8$ %), it is always in a particular context e.g. at sewage outfall (Mudge *et al.*, 1998) or within shellfish farming zones (Crawford *et al.*, 2003).

The combination of a higher sedimentation rate (Grenz *et al.* 1992) and higher POC values in the sediment (Figure 5a) ensure a much higher OM flux at C5 than at C4. The variations of the Hydrogen Index (HI) values at both these sites also reflect differences in OM composition. While the significance of POC content is straightforward, the HI index is related to the hydrogen content of organic matter and is both dependent on its biological origin (marine and/or terrestrial) and its degradation state (Espitalié *et al.*, 1985). As generally assumed, a HI value higher than 600 mg HC g^{-1} POC in immature sediments, represents a lacustrine material enriched in hydrocarbonaceous moieties. An organic material with a HI ranging between 300 and 600 mg HC g^{-1} POC often originates from algae (e.g. phytoplankton). Finally, a material with a HI lower than 300 mg HC g^{-1} POC is poor in hydrocarbonaceous moieties and usually represents an organic material derived from higher plants (Espitalié *et al.*, 1985; Tissot & Welte, 1984). Organic material of the two sampling stations present HI values comprised between 300 and 350 mg HC g^{-1} POC suggesting a dominant contribution from autochthonous phytoplanktonic production. However, in the top sediment layer (0-2 cm), HI values are slightly but significantly higher in C5 core than in the C4 one. This might indicate an OM content richer in hydrocarbonaceous moieties at C5 than at C4 and thus supposedly more able to sustain microbial activity.

At the C5 sampling station, the sharp POC decrease may be the result of bacterial OM assimilation or mineralisation. These processes are enhanced by the bioturbation in the surface sediment. Indeed, a mixed layer of 10 cm in thickness has been reported at the top of the core (see section 4.1). These processes easily explain why a decrease in HI values (Figure 5) is observed down to 10 cm. Moreover, OM degradation is known to favour a preferential attack of hydrogen-rich compounds (Anderson and Johns, 1986). In addition, DOC is considered as an OM degradation product (Chang and Berner, 1999). Thus, high DOC fluxes measured in Summer at C5 may attest a high OM degradation rate. All these processes may explain this sharp HI decrease and the resulting high nutrient availibility.

In contrast, at the C4 site, the surface mixed layer (0-3 cm), exhibits constant POC and HI values. This confirms the refractory property of OM and/or the balance between OM degradation and OM buried in sediments. Below 3 cm depth, a concomitant and progressive decrease in POC and HI values may result from a slight consummation of OM by microbial community through diagenesis. To conclude, in contrast to C4,, analyses at C5 revealed both stronger bacterial activities enhanced by the availability of nutrients and a thicker mixing layer implying significant OM oxidation. DOC fluxes increase as a result of OM degradation.

Global OM quantitation and characterisation by POC and HI measurements have been supplemented by neutral carbohydrate analysis. Carbohydrates are usually present in lower quantities in phytoplankton (and bacteria) than in land plants where they are dominant especially as structural components, namely cellulose, hemicelluloses and pectin. However, in all cases they present the advantage of being easily metabolisable that makes them good tracers of microbial activity. The rather low carbohydrate content of the studied sediments indicates that these compounds have most probably been already actively recycled in the water column.

The major possibilities of distinction of potential OM sources through neutral carbohydrate analysis are summarized in Table 4. Accordingly, the high levels of rhamnose (followed by fucose) in the upper C5 sediment layers were attributed to heterotrophic microorganisms that developed in bottom waters, mostly at the expense of the primary production (mainly diatoms and cyanaobacteria). The decrease of rhamnose in the sediment was attributed to an easier recycling of the microbial material than that of the primary production, fucose included. Similar features than in the C5 core have recently been observed in an eutrophic lake (Ogier *et al*., 2001). Indeed, the predominance of non ubiquitous dominant compounds such as fucose and rhamnose, strongly suggest an autochthonous organic production from phytoplankton and/or bacterial material (e.g. Moers *et al.,* 1990). Therefore, quantitation as well reactivity of OM, through carbohydrates analysis depict a higher OM accumulation and also more biodegradable OM at the C5 station than in C4. Thus, the rapid turn-over of autochthonous OM (phytoplancton, oysters-mussels feces, micro-organisms...) should impact the dissolved exchange processes at the sediment water interface of the Thau lagoon.

4.3 Diffusive nutrients fluxes, relationship with sedimentary OM load

Whatever the season, calculated diffusive fluxes values were always higher at C5 station than at C4. In summer (June 2003) at C5, diffusive nutrients fluxes were 10 times higher than at other seasons. This could be primarily explained by the quantity and the quality of the OM buried in the sediments. Others flux measurements, in summer, in an area also subject to biosediment deposition, did not give such high fluxes values (Mesnage 1994). Furthermore, concentrations gradients existed in sediments but not in the bottom waters, except in summer (Metzger *et al.* accepted, 2005). The later discrepancy could probably be explained by the fact that our porewater survey (retrival of dialyser sampler) occurred one month later after that of Metzger *et al.* (accepted, 2005).

Combined with the prevailing high temperatures, low wind and limited water circulations, the nutrient gradient in the bottom waters can be taken as an indicator of the dystrophic status of the ecosystem preceding the onset of an anoxia episode ("malaigues"). In addition, oyster farming zone A (Fig. 1) is little exposed to the winds. The water exchange between the lagoon and the Mediterranean Sea is limited by two narrow mouths and drained by numerous, small temporary rivers. These hydrologic conditions create a weak renewal of water in the Thau lagoon (Bacher *et al*., 1996), insufficient to remove the organic matter (feces, pseudo-feces) produced by oysters. The impact of oyster farming installations on the sedimentation rate and current speed has been demonstrated and evaluated. Previous studies have shown that biodeposits increased the sedimentation rate and that current speed can be reduced by around 60 % (Grenz *et al.* 1992). Recent modelling of anoxia crisis in the Thau Lagoon, has defined the main controlling factors : wind speed and the presence of oyster tables (Chapelle *et al*., 2001). Moreover, the anaerobic degradation of organic oyster biodeposits is enhanced by the semi-enclosed area (lower current efficency) and the increase of the water column temperatures during Spring and Summer months. Trophic status as well as nutrient gradients in the bottom waters depict the particular situation preceding an anoxia crisis. As mentioned above, such a crisis effectively occurred with a high intensity, in August 2003, in the Thau Lagoon.

5. Conclusion

Higher deposition rate and higher OM concentration both under the particulate (POC) and the dissolved form (DOC), entail greater OM fluxes at the C5 station in the shellfish production zone, than at the C4 site in open waters. The geochemical discrepancy between both these two sites is true whatever the season and could be, at least primarily, simply explained by the contribution of oyster feces to sediment load.

The Hydrogen Index that gives a rough estimate of quality of the OM depicts a material richer in hydrocarbon and more biodegradable at C5 station than at C4. This is also in agreement with the porewater chemistry which revealed nutrients fluxes to be always 10 times higher at C5 than at C4. Neutral carbohydrate analysis confirms the labile character of OM in the surficial sediment at this site (C5). Indeed, fucose and glucose, the main carbohydrates measured in the surficial sediments suggest *in situ* phytoplanktonic production to be the main OM source.

Porewater profiles revealed the trophic status at the C5 station At C5, nutrient profiles showed a deep seasonal variation between winter and summer. Sharp gradients that have been evidenced below the sediment-water interface also extended above, in the bottom waters, in summer. The presence of such nutrients gradients at the bottom of the water column, in June 2003, is an indication of an impending anoxia crisis, which occured in August 2003 immediately after our field survey.

All our results (on particulate and dissolved organic species) point to a biogeochemical gradient between the C5 and C4 stations. Indeed, nutrients exchange dynamic is higher at C5 station, proving the impact of oysters farming in the buried labile OM. With its rapid turn-over, *in situ* OM production controls nutrients exchange at the sediment-water interface.

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Table 1

Temperature and porosity used in the flux calculation

Sampling date	January		April		June	
Sampling station	C4	C5	C4	C5	C4	C5
Temperature (°C)	4	4	8	8	15	15
Porosity	0.61 ± 0.03	0.69 ± 0.06	0.71 ± 0.07	0.73 ± 0.013	0.43 ± 0.01	0.43 ± 0.01

Table 2

Calculated diffusiv fluxes of Nutrients (N, P), nm : not measured

Sampling date	January		April		June	
Sampling station	C4	C5	C4	C5	C4	C5
$Js(NH_4^+)$ mmol.m^{-2}.d^{-1}	+0.2 ± 0.05	+0.62 ± 0.1	0.05 ± 0.01	+1.0 ± 0.1	nm	+10.7± 0.3
$Js(PO_4^{3-})$ mmol.m^{-2}.d^{-1}	+ 0.03 ± 0.01	+ 0.3 ± 0.07	+ 0.02 ± 0.02	+0.14± 0.02	nm	+0,96 ± 0.07

Table 3a

Rock-Eval index (POC and HI) and neutral carbohydrate composition of sediment C5 core samples

Rock-Eval			Total neutral carbohydrate (%)							Total	TCH2O
Depth (cm)	POC (%)	HI (mg HC / g POC)	Arabinose	Rhamnose	Fucose	Mannose	Galactose	Xylose	Glucose	(mg/g sed.)	(mg / 100 mg POC)
0-0.5	4,4	367	7,9	22,6	22,0	8,0	10,2	10,5	18,8	3,59	8,26
0.5-1	4,1	378	9,4	28,4	21,9	6,2	7,6	11,6	14,9	3,04	7,46
1-1.5	3,9	372	7,4	24,6	17,5	8,4	17,6	11,2	13,4	3,23	8,37
1.5-2	3,3	372	10,0	22,4	22,0	9,0	11,4	13,5	11,6	3,20	9,81
2-3	3,3	364									
3-4	3,2	359									
4-5	2,9	372									
5-6	2,7	360									
6-7	2,4	351									
7-8	1,7	323									
8-9	1,9	311									
9-10	2,2	217									
10-11	1,9	245									
11-12	2,0	279									
12-13	2,3	235									
13-14	1,8	276	23,7	17,9	34,8	4,3	3,7	8,6	7,0	2,23	12,4
14-15	1,6	335	7,7	20,6	18,3	13,0	7,3	15,4	17,7	1,46	9,04
15-16	2,2	260	21,2	19,5	30,3	3	4,4	7,95	13,7	1,9	8,5
16-17	1,7	305	10.3	16.6	19,9	10,4	14,4	13	15,4	1,6	9,4
17-18	1,5	324	14	21.7	26,5	9,9	6,5	8,1	13,2	1,5	9,8
18-19	1,9	246	7.6	12.4	15,2	14	16,4	14,9	19,5	1,6	8,2
20-21	1,8	258	14.3	26.7	23,3	6	6,3	13,5	9,8	1,2	7

Table 3b

Rock-Eval index (POC and HI) and neutral carbohydrate composition of sediment C4 core samples

	Rock-Eval		Total neutral carbohydrate (%)							Total	TCH2O
Depth (cm)	POC (%)	HI (mg HC / g POC)	Arabinose	Rhamnose	Fucose	Mannose	Galactose	Xylose	Glucose	(mg/g sed.)	(mg / 100 mg POC)
0-0.5	3,0	354	8,9	1,8	29,0	9,6	13,2	13,2	24,5	2,52	8,41
0.5-1	3,0	347	14,4	8,9	18,1	10,1	11,5	13,8	23,2	2 ,09	6,87
1-1.5	3,2	341	12,0	13,8	22,5	9,6	11,7	8,0	22,4	2 ,52	8,01
1.5-2	3,2	352	7,3	8,6	16,6	10,2	15,1	18,0	24,3	1,70	5,35
2-3	3,1	338									
3-4	2,9	342									
4-5	2,7	353									
5-6	2,8	333									
6-7	2,7	336									
7-8	2,5	336									
8-9	2,6	317									
9-10	2,6	307									
10-11	2,6	314									
11-12	2,8	315									
12-13	3,1	304	14,6	14,0	25,8	8,2	7,8	14,1	15,6	1,81	6,89
13-14	3,0	319	0,9	15,6	15,9	9,4	18,0	12,0	28,2	2,52	9,12
14-15	3,1	286	6,8	17,8	17,7	9,3	13,0	12,0	23,5	3,17	10,33
15-16	3,8	264	6,3	11,8	15,1	10,0	15,5	14,4	27,0	3,23	10,67
16-17	2,7	306	6,7	15,7	15,2	10,6	16,9	12,5	22,4	3,03	9,77
17-18	2,7	303	10,7	19,8	19,8	6,6	9,1	17,7	16,3	2,31	6,09
18-19	2,6	354	10,4	16,2	23,2	5,5	13,3	14,8	16,7	2,15	7,93
20-21	2,8	347	10,2	21,3	17,3	12,5	15,4	15,5	7,9	2,27	8,39

Table 4

Literature sources for Potentiel sources of OM, through Neutral Carbohydrate association

Potential sources	Neutral carbohydrate association	Réferences
Terrestrial plant tissues	Arabinose, Mannose, Galactose, Xylose and Glucose	Sjöström, 1981
Bacteria	Rhamnose, Fucose and glucose	Barkers & Somers, 1970 Boon et al., 1983 Bhosle et al., 1983 Hicks et al., 1994 Ogier et al., 2001 Weckesser & Drew, 1979
Phytoplankton Diatoms	Glucose and Fucose	Percifal, 1970 Cowie & Hedges, 1984 Meeuse, 1962 Bölter & Dawson, 1982 Hecky *et al*., 1973 Moers *et al*., 1990 Tanoue & Handa, 1987

Figures Caption -

Figure 1 : Location of the study site : the « Thau » Lagoon (France).

Figure 2 : Porewater profiles of Soluble Reactiv Phosphate (SRP) versus depth at the C5 sampling station (a) in winter, (b) in spring, (c) in summer; and at the C4 sampling station (d) in winter, (e) in spring. Two diffusion samplers have been deployed at each season and sampling station giving two profiles except in winter at C5 (a).

Figure 3 : Porewater profiles of ammonia (NH_4^+) versus depth at the C5 sampling station (a) in winter, (b) in spring, (c) in summer; and at the C4 sampling station (d) in winter, (e) in spring. Two diffusion samplers have been deployed, giving two profiles, at each season and sampling station except in winter and spring at C5 (a, b), in winter at C4 (d).

Figure 4 : Porewater profiles of Diossolved Organic Carbon (DOC) versus depth at the C5 sampling station (a) in winter, (b) in spring, (c) in summer; and at the C4 sampling station (d) in winter, (e) in spring. Two diffusion samplers have been deployed at each season and sampling station.

Figure 5 : POC (%) and HI (mg HC g^{-1} POC) at the C5 station (a), and at the C4 station (b).

Figure 6 : Average weight percentages of individual neutral carbohydrates, in C5, (a) at the surficial sediment (0-2 cm) and (c) at the end of the core (13-22 cm); and in C4, (b) at the surficial sediment (0-2cm) and (d) at the end of the core (10-20 cm).

Figure 1 : Location of the study site : the « Thau » Lagoon (France)

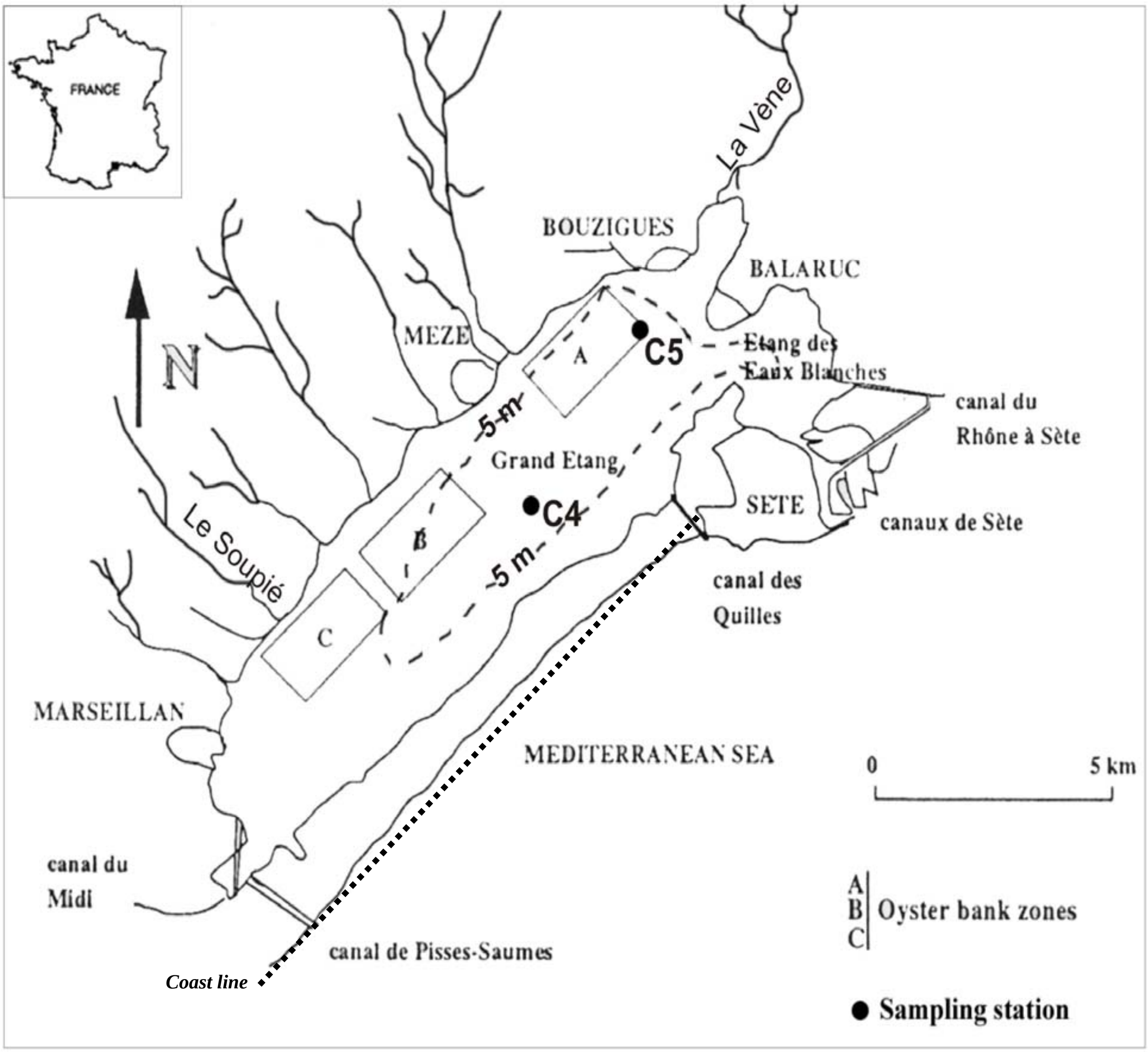
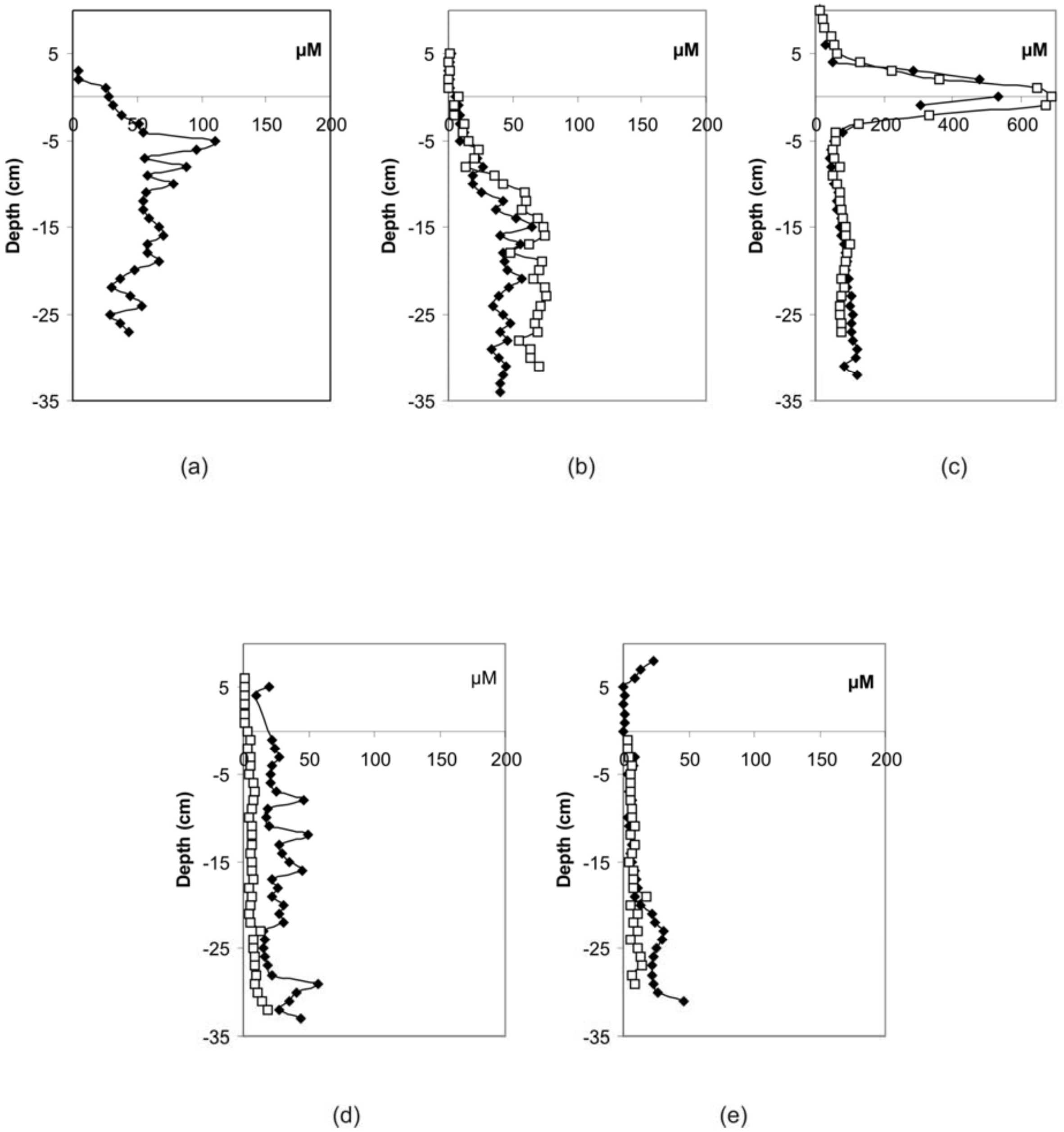


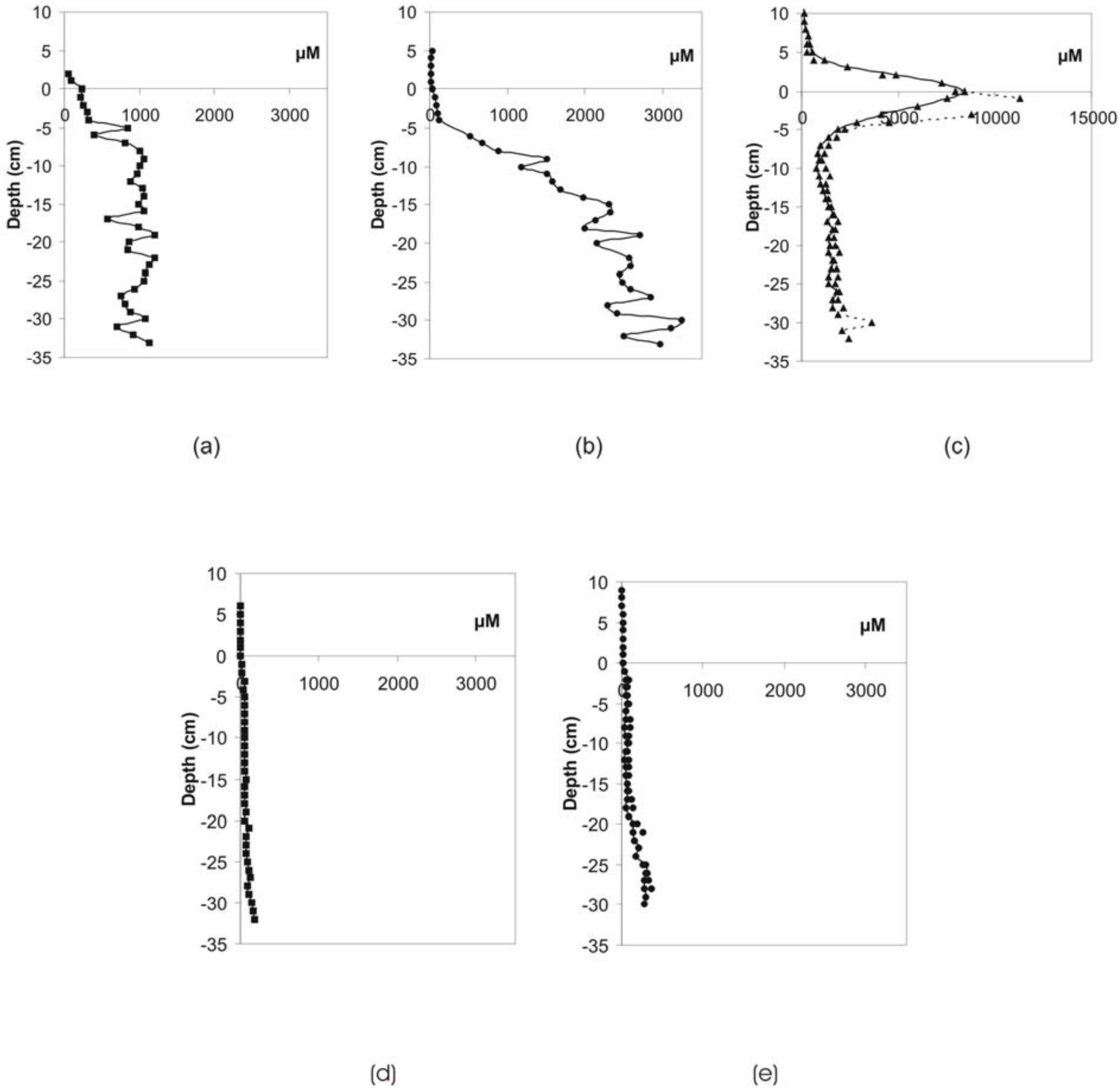
Figure 2 : Porewater profiles of Soluble Reactiv Phosphate (SRP) versus depth at the C5 sampling station (a) in winter, (b) in spring, (c) in summer; and at the C4 sampling station (d) in winter, (e) in spring. Two diffusion samplers have been deployed at each season and sampling station giving two profiles except in winter at C5 (a).



(a) (b) (c)

(d) (e)

Figure 3 : Porewater profiles of ammonia (NH_4^+) versus depth at the C5 sampling station (a) in winter, (b) in spring, (c) in summer; and at the C4 sampling station (d) in winter, (e) in spring. Two diffusion samplers have been deployed, giving two profiles, at each season and sampling station except in winter and spring at C5 (a, b), in winter at C4 (d).



(a) (b) (c)

(d) (e)

Figure 4 : Porewater profiles of Diossolved Organic Carbon (DOC) versus depth at the C5 sampling station (a) in winter, (b) in spring, (c) in summer; and at the C4 sampling station (d) in winter, (e) in spring. Two diffusion samplers have been deployed at each season and sampling station.

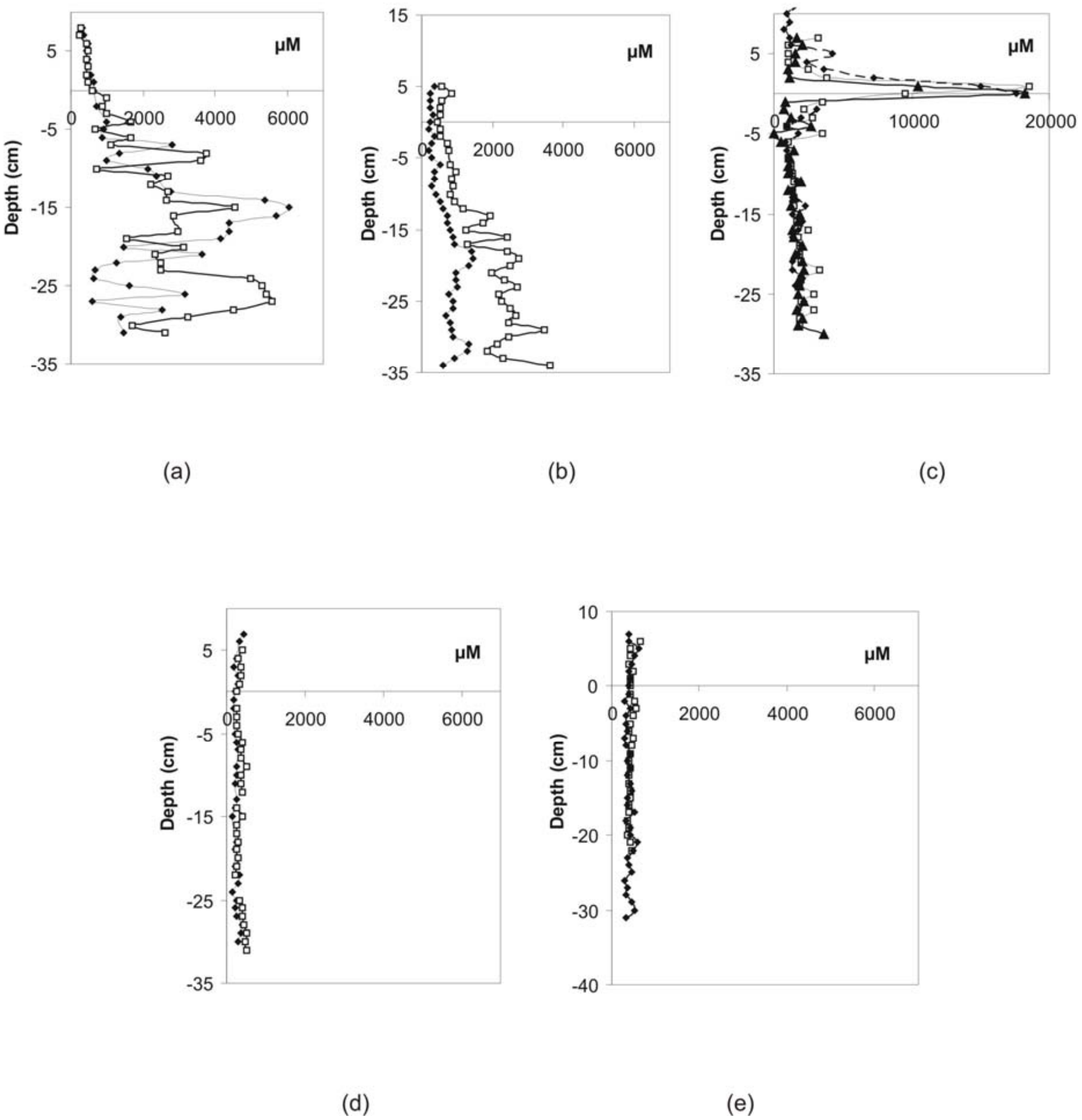


Figure 5 : POC (%) and HI (mg HC g^{-1} POC) at the C5 station (a), and at the C4 station (b)

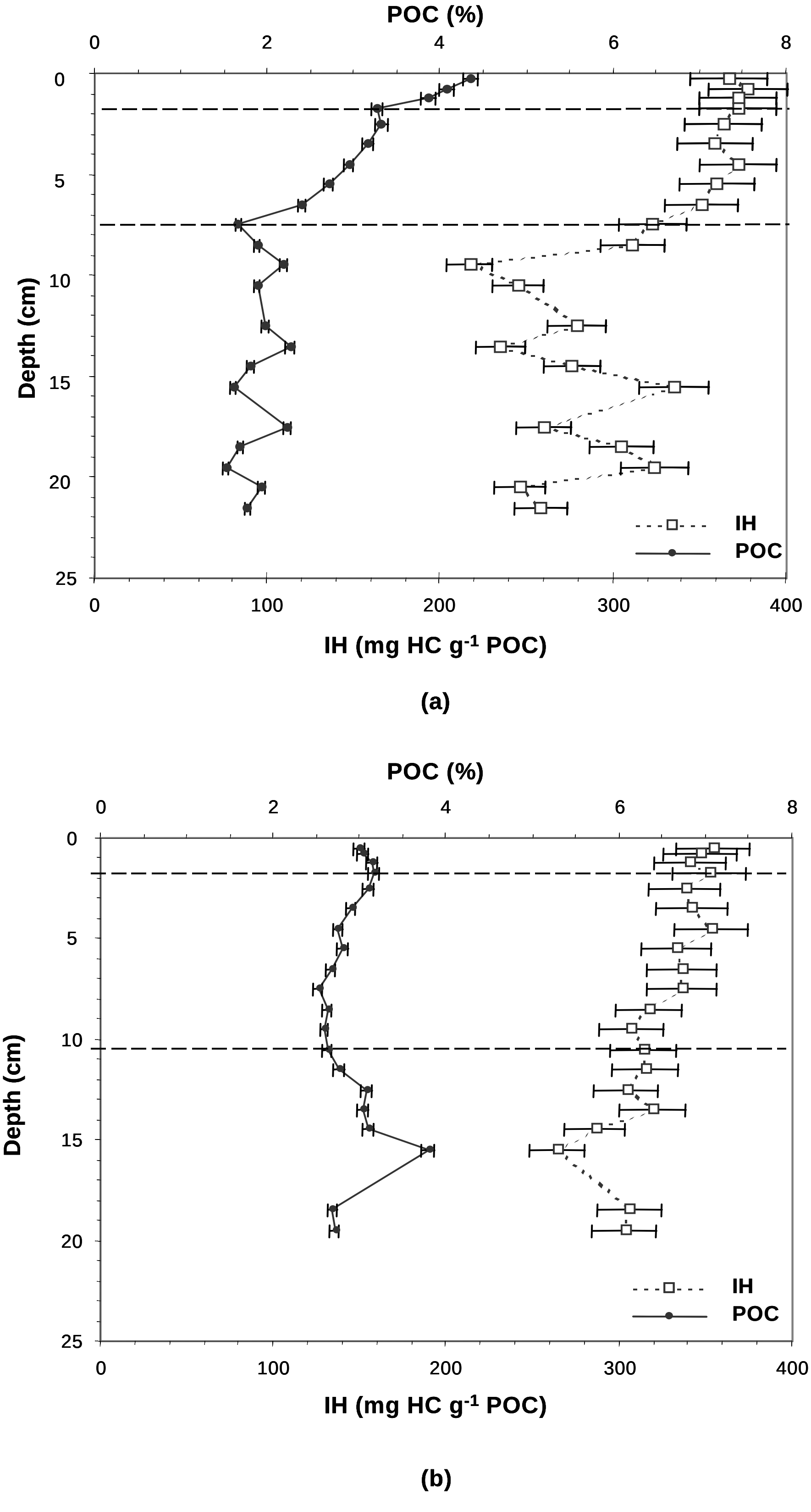
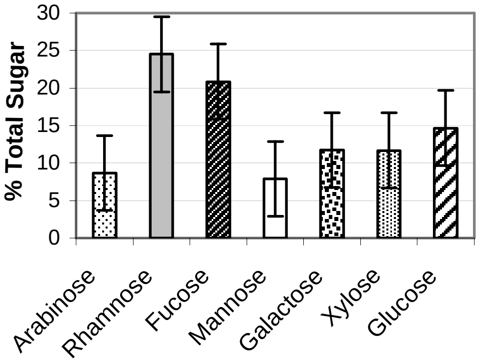
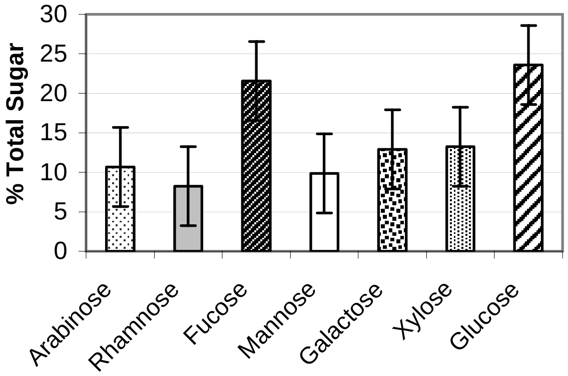


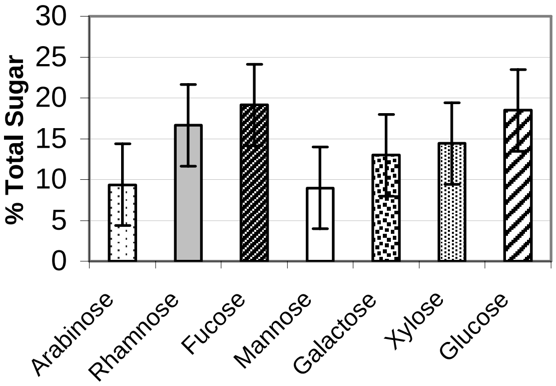
Figure 6 : Average we (0-2 cm) and (c) at the end of th the core (10-20 cm).


% Total Sugar
30
25
20
15
10
5
0
Arabinose
Rhamnose
Fucose
Mannose
Galactose
Xylose
Glucose

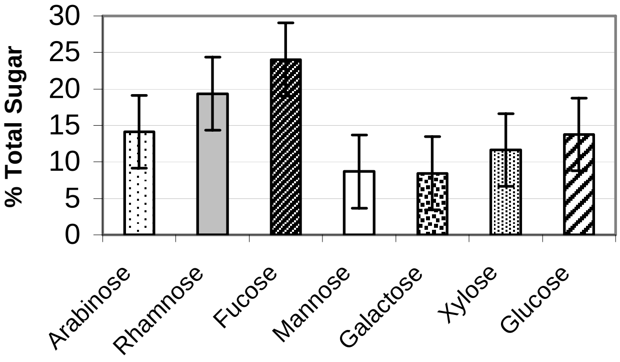
(a)


% Total Sugar
30
25
20
15
10
5
0
Arabinose
Rhamnose
Fucose
Mannose
Galactose
Xylose
Glucose

(b)


% Total Sugar
30
25
20
15
10
5
0
Arabinose
Rhamnose
Fucose
Mannose
Galactose
Xylose
Glucose

(c)


% Total Sugar
30
25
20
15
10
5
0
Arabinose
Rhamnose
Fucose
Mannose
Galactose
Xylose
Glucose

(d)