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Biogeochemical and contaminant cycling in sediments from a human-impacted coastal lagoon – Introduction and summary

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1. General purpose

A general decrease in the anthropogenic pressure on coastal ecosystems has been observed recently in developed countries. But coastal lagoon ecosystems are still undergoing major human impact (Lotze *et al.*, 2006). A major environmental concern is the enhancement of contaminant dispersion and algal production due to eutrophication, associated with an increase in the duration of intermittent seasonal periods of anoxia. Due to past industrial activity, large concentrations of contaminants have been accumulated in sediments of natural water bodies. One of the issues raised by environmentalists is the fate of these contaminants with changing environmental conditions, such as restoration of water bodies to their "pristine" state (water framework directives), or worsening of the environment due to climate change and nutrient/organic loading. The processes that govern the fate of contaminants in sediments are complex interactions with the biogeochemical cycles of major red-ox and biogenic elements, such as C, O, P, S, Si, Fe, Mn. Coupled together with the sources (rivers, water table, surface runoff, atmospheric precipitation), and physical constraints of the water column, the biogeochemical dynamics in the sediment ultimately controls the variation of contaminant sources over inter-annual time scales. In the sediments, microbial and phytobenthic activity promotes changes in oxidation state of porewaters and sediment, in porewater pH, in reduced chemical species, which modifies the recycling of carbon and nutrients, and alters the mobility of contaminants in sediments.

From 2001 to 2003, the Microbent project ("Biogeochemical processes at the water-sediment interface in eutrophic environment") was carried out within the framework of the Programme National Environnement Côtier, the French contribution to Land Ocean Interaction in the Coastal Zone (LOICZ).

The Microbent programme was focused on the study of sediment biogeochemical cycles of carbon, oxygen, sulphur, iron, nitrogen, and phosphorus in relation to the faunal activity in the sediment and their relation with the mobility of metallic contaminants at the sediment-water interface (SWI) in a Mediterranean coastal lagoon (Thau Lagoon, France; Fig. 1). The aim of Microbent was to set up an interdisciplinary study bringing together geochemists, sedimentologists, and biologists in order to understand and quantify the main reaction pathways, and the fluxes of contaminants at the SWI, including those related to benthic fauna. Work was focused on the processes which generate contaminant fluxes: (i) early diagenesis processes, which generates the chemical conditions of the environment, (ii) processes leading to the transfer of contaminants from particles towards biofilms, water column, and organisms, (iii) processes of sediment mixing by organisms and sediment accumulation.

2. Summary of major results

2.1. Study site

The Thau lagoon is a shallow and microtidal coastal enclosed bay exposed to human activity (Fig. 1). The surface area of the Thau lagoon is about 75 km², the mean depth 3.5 m and the maximum depth 11 m. Salinity varies between 31 and 39. Twenty percent of the surface is occupied by shellfish farming with a total production reaching 22,000 tons a year, mainly oysters *Crassostera gigas,* and mussels *Mytilus galloprovincialis*.

Sampling site C4 is located at a central position in the lagoon (N 43°24.018, E 3°36.703). Around this position, the station represents a circle of 100 meters in diameter and is at a depth of 8 meters. The station C5 (N 43°25.994, E 003°39.657) is located close to a mussel table, where organic carbon fluxes are higher. The C5 working area is about 10 m in diameter and the water column height is 9 m. Five campaigns were undertaken in order to document seasonal trends between December 2001 and May 2003 (M1: Dec 2001and Jan 2002 M2: Apr 2002; M3: Aug 2002; M4: Jan 2003; M5: May 2003).

2.2. Overview of the early diagenesis processes

A combination of techniques was used to obtain an overall view of early diagenesis processes at the two main stations. Pore water extraction from sediment cores and *in situ* pore water sampling with dialysis devices (Metzger *et al.*, Anschutz *et al.*) enabled us to determine the centimetre scale vertical distribution of dissolved species across the sediment water interface, including major cations (sodium, potassium, magnesium, calcium), minor cations (lithium, strontium, barium), redox sensitive species (dissolved manganese, ferrous iron, sulphate, sulphide, ammonium, nitrate) and other diagenetic parameters (pH, alkalinity, soluble reactive phosphorous, dissolved silica). The high resolution distribution of dissolved oxygen and pH was acquired using in situ microsensors (Dedieu *et al.*). To complement the 1D analysis of porewaters, we used a new sediment 2D planar probe for measuring dissolved iron and sulphur, a device that is a combination of a DET (Diffusive Equilibration in Thin-films) device and a DGT (Diffusive Gradients in Thin films) device (Jezequel *et al.*). Direct flux measurements of dissolved species across the sediment-water interface were obtained by in situ incubation using benthic chambers (Thouzeau *et al.*).

The data collected from the Thau lagoon sediments followed a general sequence of early diagenetic reactions (Froelich *et al.*, 1979; Emerson and Hedges, 2003) in which oxygen was reduced near the sediment-water interface, followed by the reduction of iron oxides, and sulphate, whereas reduced compounds accumulated in the sediment. However, a large difference was observed between the two main stations which were located in the center of the lagoon (C4) and close to the oyster/mussel farm (organically enriched, C5). The organic enrichment linked to oyster farming was clearly visible on oxygen distributions and fluxes and lead to an increased intensity of diagenesis (Fig. 2).

Oxygen profiles penetrated twice as much at the central site compared to the organically enriched (3-5 mm compared to 1-2mm, Dedieu *et al.*). The effect of this different organic load was apparent in the exchange fluxes which were measured using benthic chamber. Oxygen fluxes were doubled near the oyster farm compared to the centre of the lagoon (45 versus 20 mmol m^{-2} d^{-1}, Thouzeau *et al.*). Sulphate reduction rates also differed between the two stations in the same proportion as the oxygen fluxes (20 mmol m^{-2} d^{-1} near the oyster farm versus 10 mmol m^{-2} d^{-1} in the central part of the lagoon, Point *et al.*). These rates and oxygen distribution translated in very different depth scale of the diagenetic sequence (Metzger *et al.,* Anschutz *et al.*). In the central zone, the oxic and suboxic zones spread over 15-35cm depending on exact location and season with the anoxic sulphidic zone starting around 20 cm depth, whereas the organically enriched site showed a rapid growth of sulphide concentrations below 3-5 centimetres. Therefore, the two stations (C4 and C5) displayed contrasted diagenetic situations which were favourable to the study of trace metal mobility (Fig. 2). Indeed, trace metals speciation is dependent on redox conditions, sulphide concentration, and the presence of iron or manganese oxides. In this regard, small scale variability within the different sites was evidenced by the presence of micro niches with specific bacterial activities using the 2D sensors of dissolved Fe(II) and S(-II) (Jézéquel *et al.*). This variability may create hot spots of mobility/trapping of trace metals which may locally alter the contaminant transfer.

Most studies presented in this volume focused on spatial and temporal variability of the benthic system. The drivers of seasonal variation of the oxygen uptake and DIC fluxes were identified: temperature variation (a difference of 15-20°C between winter and summer, with a Q10 of 2.5), labile organic matter availability and the presence/absence of the macroalgal cover on the sediment (Dedieu *et al.*).

Nitrate reduction was very low as both nitrate concentrations in the water column (around 1µM) and nitrification rates were insignificant. Concerning the phosphorus cycling, the precipitation of an authigenic phosphorus-bearing phase was proposed at the station near the oyster park (Anschutz *et al.*). This suggested that the sediment located below the shellfish farming tables acted as a sink for lagoon phosphorus. Profiles of dissolved calcium also showed that the anoxic sediment of the Thau lagoon is a location for calcium carbonate precipitation (Metzger *et al.*). Sediment porewaters were supersaturated with respect to calcite because of the alkalinity increase caused by sulphate reduction. The precipitation of authigenic calcite in the shallow Thau lagoon sediments suggested that this process probably plays a role in the carbon balance of coastal environment.

2.3. Mobilization and remobilization of trace metals at the sediment-water interface (SWI)

Coastal sediments in industrialized area have been impacted by metallic contaminants which have been stored in sediments, with capability for remobilization, exchange with the water column and a possible transfer to the benthic and pelagic food webs. Different techniques such as in situ probes, benthic chambers and field and laboratory experiments have enabled the investigation of the reactivity and cycling of trace elements at the sediment-water interface. Using the gradient in diagenetic conditions (see above section), these studies illustrate the role of redox and diagenetic processes, microscopic and macroscopic biological activities in mediating benthic reactivity and exchanges of trace metals.

Benthic chamber fluxes were measured for redox sensitive trace metals (Cu, Pb, Co). They exhibited a significant correlation with Mn fluxes (Point *et al.*) which can be used as a proxy for such suboxic to anoxic remobilisation processes at the SWI in eutrophic benthic environments (Table 1). In the example of Table 1, the Mn fluxes show an opposite sign between the organic-rich site (C5) which was a source of Mn for the water column and the central zone (C4) which was a slight sink. Cu, Pb or Co display a similar behaviour as Mn, with the organic-enriched zone being mostly a source of these metals and the low impact zone being mostly a sink. The uranium flux displayed a negative correlation with Mn fluxes. Indeed, processes dominating uranium behaviour are linked to sulphate reduction which acts as a sink for uranium by reducing the U-oxydes and uranium flux entering the sediment was found to be positively correlated with sulphate reduction rates measured within the first centimetre of the top sediment layer (Point *et al.*). Such coastal sediments act as a uranium sink related to the intense microbial activity located in the upper sediment layers.

Cadmium displayed a different behaviour with a similar flux in the two diagenetic situations (C4 and C5). In sediments, suboxic to anoxic conditions lead to sequential immobilisation of dissolved cadmium by sulphide production whereas production of dissolved Cd is linked to the reductive dissolution of iron and manganese oxyhydroxides. This was investigated in surface sediments during contrasted seasonal campaigns for both the reference and the mussel farm sites using DGT and DET combined probes (Metzger *et al.*). These two opposite processes lead to little variation in dissolved Cd fluxes between the two sites despite the very different diagenetic intensities (Point *et al.*) suggesting that production and consumption processes were counterbalancing each other. The comparison between calculated diffusive fluxes (Metzger *et al.*) and benthic chamber fluxes (Point *et al.*) suggested the major contribution of advective processes in surface sediment, enhancing Cd mobilisation. In addition, Cd presented the highest lability (compared to Cu and Zn) toward benthic bivalves and worms, and exhibited a proportional gradient between sediment contamination and bivalve bioaccumulation (Amiard *et al.*).

Partition, mobility and fluxes of total mercury and methylmercury were investigated on sediment, porewaters and overlying water (Point *et al.,* Muresan *et al.,* Montperrus *et al.*). In Table 1, total dissolved Hg showed a good correlation with Mn whereas Methyl mercury showed a weak negative correlation. Investigation of diagenetic processes (Muresan *et al.*) indicated that amorphous iron oxyhydroxides play a major role in controlling total mercury at the SWI, whereas HgT was in equilibrium between solid and solution in the sulfidic part of the cores. Calculated diffusive fluxes for total mercury (Muresan *et al.*) exhibited intensities 20 to 100 times lower compared to measured benthic chamber fluxes (Point *et al.*). These results indicate again that significant advective transport is involved in benthic exchanges of both mercury species**.** In addition, potential mercury methylation studies in surface sediments were performed under spring conditions. They exhibited complex pathways for methyl mercury formation as influenced by both benthic and pelagic dynamics (Monperrus *et al.*), which explains the lack of relationship between methyl mercury and Mn fluxes.

The intensity of benthic remobilisation of most trace metals and organometals was found to be strongly driven and enhanced by macrofaunal density and potential activity (irrigation, reworking, and ingestion). Processes governing benthic exchanges and bioaccumulation of trace metals remain complex and results obtained for methylmercury and tributyltin benthic fluxes (Point *et al.*) or Zn and Cu bioaccumulation (Amiard *et al.*) demonstrate that further processes need to be considered and investigated. For example**,** additional experiments with benthic chambers with macroalgal cover demonstrated significant changes in benthic fluxes intensity and direction for all redox sensitive trace metals between dark and light conditions (Point *et al.*). This result suggests that benthic metal processes may vary over diurnal time scale in shallow coastal environment.

2.4. Sedimentation, bioturbation and archiving

Sediment accumulation and mixing are important processes which govern the distribution and fate of particulate chemical elements before their archiving in the sediment column. These processes were investigated at the two stations using complementary analyses of radionuclides (^{234}Th, ^{7}Be and ^{210}Pb, Schmidt et al.), fluorescent particles (luminophores) and macrofaunal population (Duport et al.), which allowed the quantification of sedimentation and bioturbation rates. A seasonal model describing biotubation and burial was specially designed to account for temporal variations of these processes and the deposition fluxes of radionuclides (Lecroart *et al.*).

As exemplified in the papers from Schmidt *et al.* and Duport *et al*., no significant differences between the two stations were found in the intensity of overall sediment reworking for both radionuclides and luminophores measurements.

Yet, the two contrasted site with different organic loading and diagenetic settings hosted different functional groups of macrobenthos. A dominance of biodiffusors was observed at the site located in the centre of the lagoon where organic loading was low whereas gallery-diffusors were predominantly recorded at the site close to the shellfish farm. Taking into account the dominant functional groups present, there was thus a higher potential in surface oxygen and suboxic conditions penetration at the low impact site due to an homogeneous and active reworking of the surface layer linked to the organisms displacements. At the organic rich site, where biogenic structures built by the organisms created irrigated spots in a scattered pattern, less efficient oxygen diffusion and solid oxidant penetration were present which explain the occurrence of sulphide at 3-5 cm

Both sedimentary ^{234}Th and ^{7}Be showed seasonal variations in activities and in penetration, up to 8 cm, which indicated efficient and variable mixing of upper sediments with time (Schmidt *et al*.). Bioturbation rates (D_b) were calculated from these profiles as a diffusive process under steady-state. Sediment reworking was also determined using the luminophore method which clearly showed that radionuclide-D_b values presented higher values than luminophores-*Db*. The two methods showed a similar trend with time, indicating seasonal variation in particle penetration and mixing within the sediment. The seasonal trend showed an increase of mixing intensity in summer which was related to the seasonal variability in functional bioturbation group composition (e.g., biodiffusors and gallery-diffusors) within the macrofaunal populations (Duport *et al*.).

By developing a time-dependent model, Lecroart *et al*. tested the accuracy of the conventional method used to calculate bioturbation coefficients from ^{7}Be and ^{234}Th profiles at steady-state. The model simulated activity profiles influenced by either seasonal or episodic input of radionuclide flux at the SWI, and calculated the apparent bioturbation coefficient. The error induced by the steady-state approximation reached significant values (up to 163 % with the ^{7}Be and 74 % with the ^{234}Th) calculated with a set of parameters typical of coastal environments.

3. Conclusions

Contaminant mobility in sediments is largely dependent on early diagenetic processes. The oxic-anoxic transition which involves changes in oxidation state of metallic contaminants and their carrier phase is essential in metal speciation. In addition, several other parameters are crucial in generating transfer and trapping of trace metals in the sediment column: the availability of iron and manganese oxyhydroxydes, the concentration of free sulphide partly controlled by reduced iron, the availability of organic substrates, the intensity of bioturbation and irrigation. Thus temporal and spatial variations of biogeochemical cycling of elements such as C, O, Fe, S imply differences in the fate of trace metals deposited or historically buried in sediments. During the Microbent programme, we showed that changes in labile organic loads in sediments (related to the shell farming activity in the Thau lagoon) and their consequences related to early diagenesis or faunal population could significantly alter the fate of trace metals in sediments such as Cu, Co, U, Pb and Hg in a non-linear way.

The results presented in this special issue show that an interdisciplinary approach, coupled to time-series investigation can provide understanding of complex benthic processes. These advances help to resolve the coupling between metallic contaminant mobility, organic matter recycling and benthic ecosystem functionality in complex coastal environments such as lagoons.

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Diagenesis

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3- Benthic response to shellfish farming in Thau lagoon : pore water signature"
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4- Two-dimensional determination of dissolved iron and sulfur species in marine sediment pore-waters by thin-films based imaging. Thau lagoon (France).
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14- Numerical estimation of the error of the biodiffusion coefficient in coastal sediments
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Table 1: Average trace metal fluxes in the two diagenetic contexts in April 2002: Intensified suboxic/anoxic conditions near the oyster farm (showed by Mn efflux) promote a release of redox sensitive metals (station C5). Positive values indicate effluxes out of the sediment whereas negative values indicate influxes from the water column.

Fluxes of	Center of the lagoon : C4	Near the oyster farm C5
Mn (µmol/m^2/d)	**-11**	**+115**
Co (µmol/m^2/d)	**-0.7**	**+3.4**
Cu (µmol/m^2/d)	**-7**	**+11**
Pb (µmol/m^2/d)	**+1**	**+4**
U (µmol/m^2/d)	**+1.7**	**-2.7**
Cd (nmol/m^2/d)	**+110**	**+110**
HgT (nmol/m^2/d)	**-3.2**	**+2.6**
MMHg (pmol/m^2/d)	**+300**	**+95**

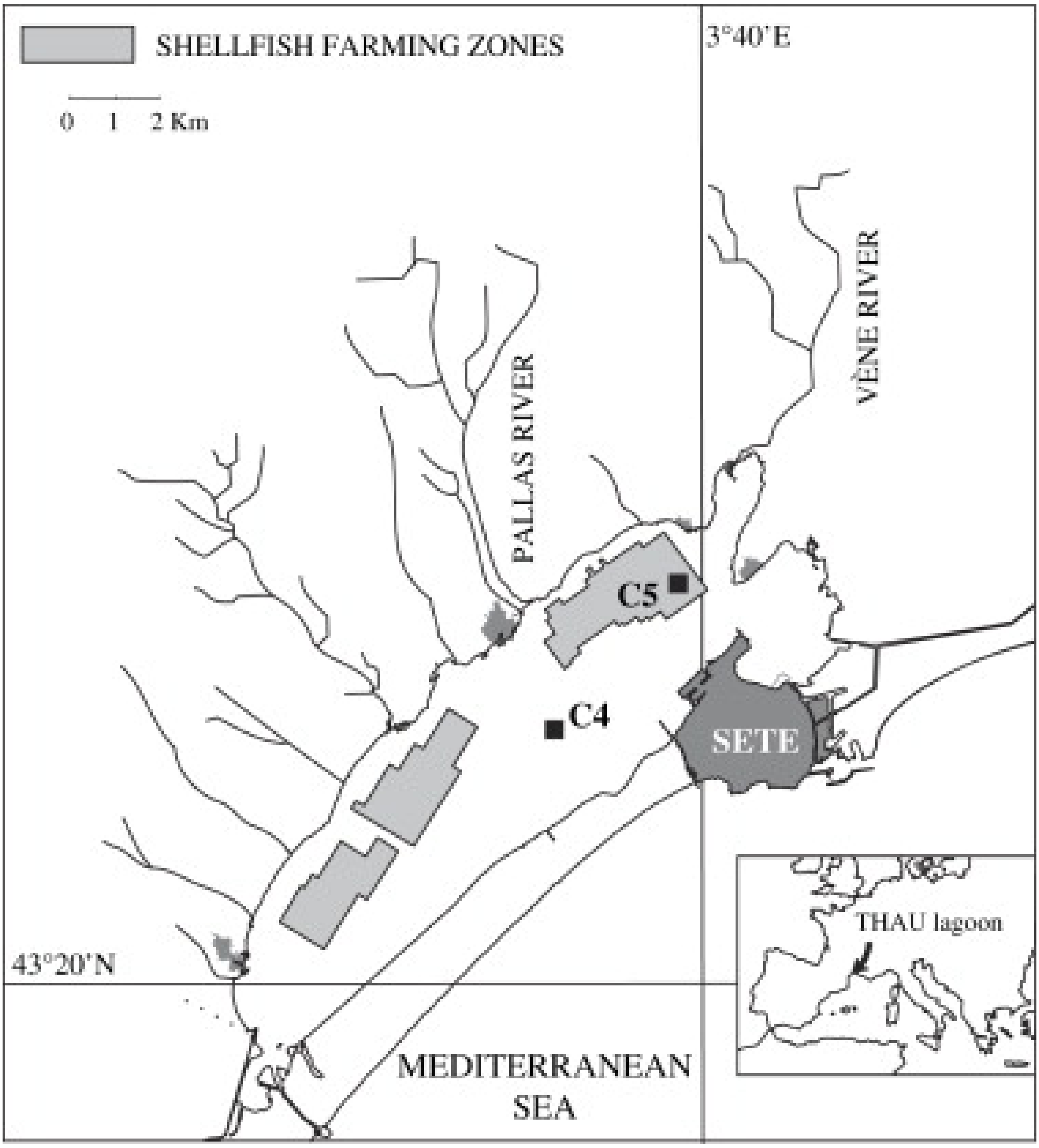

Fig. 1. Sampling site and locations of the two stations in the Thau lagoon (station C4 in the central part of the lagoon and station C5 near the shellfish farming area).

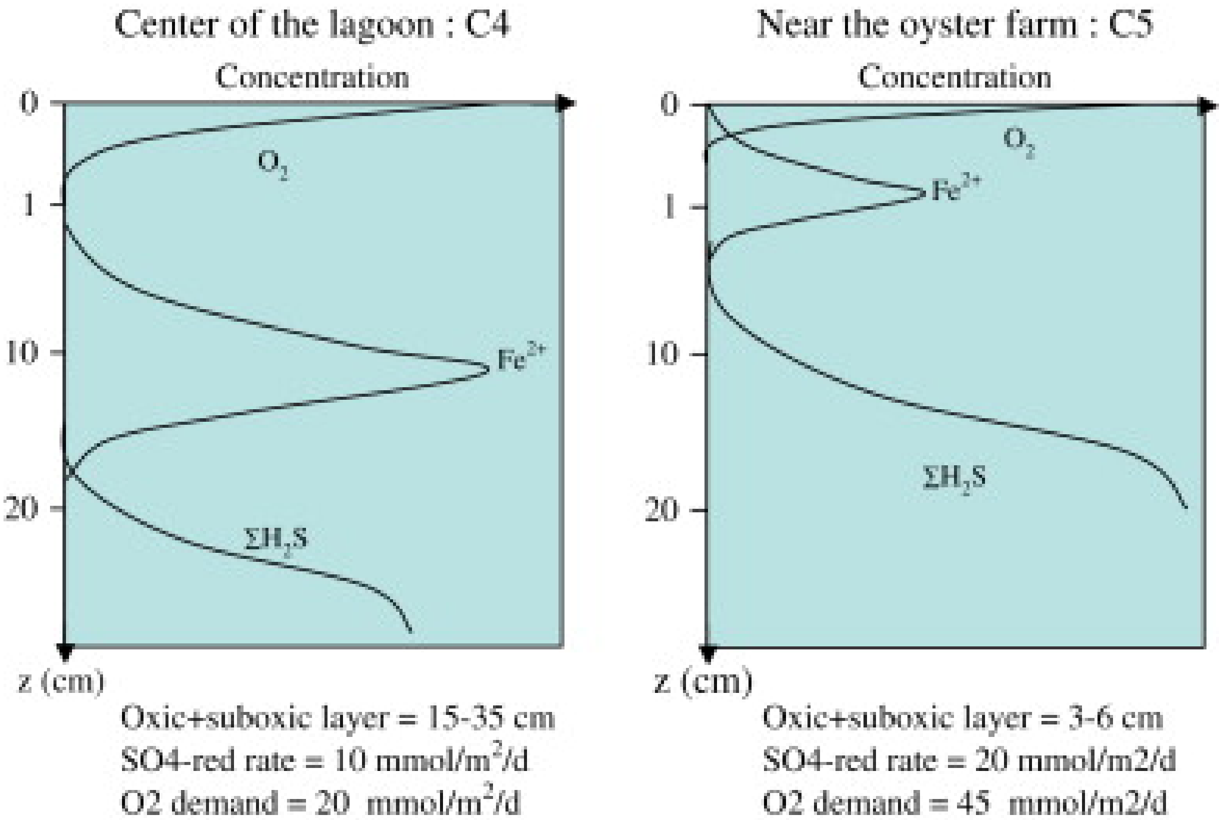

Fig. 2 : A schematic view of early diagenesis at the two sites studied in the Thau lagoon. Organic matter recycling is enhanced in the sediments of the oyster farm leading to reduced conditions close to the sediment-water interface.

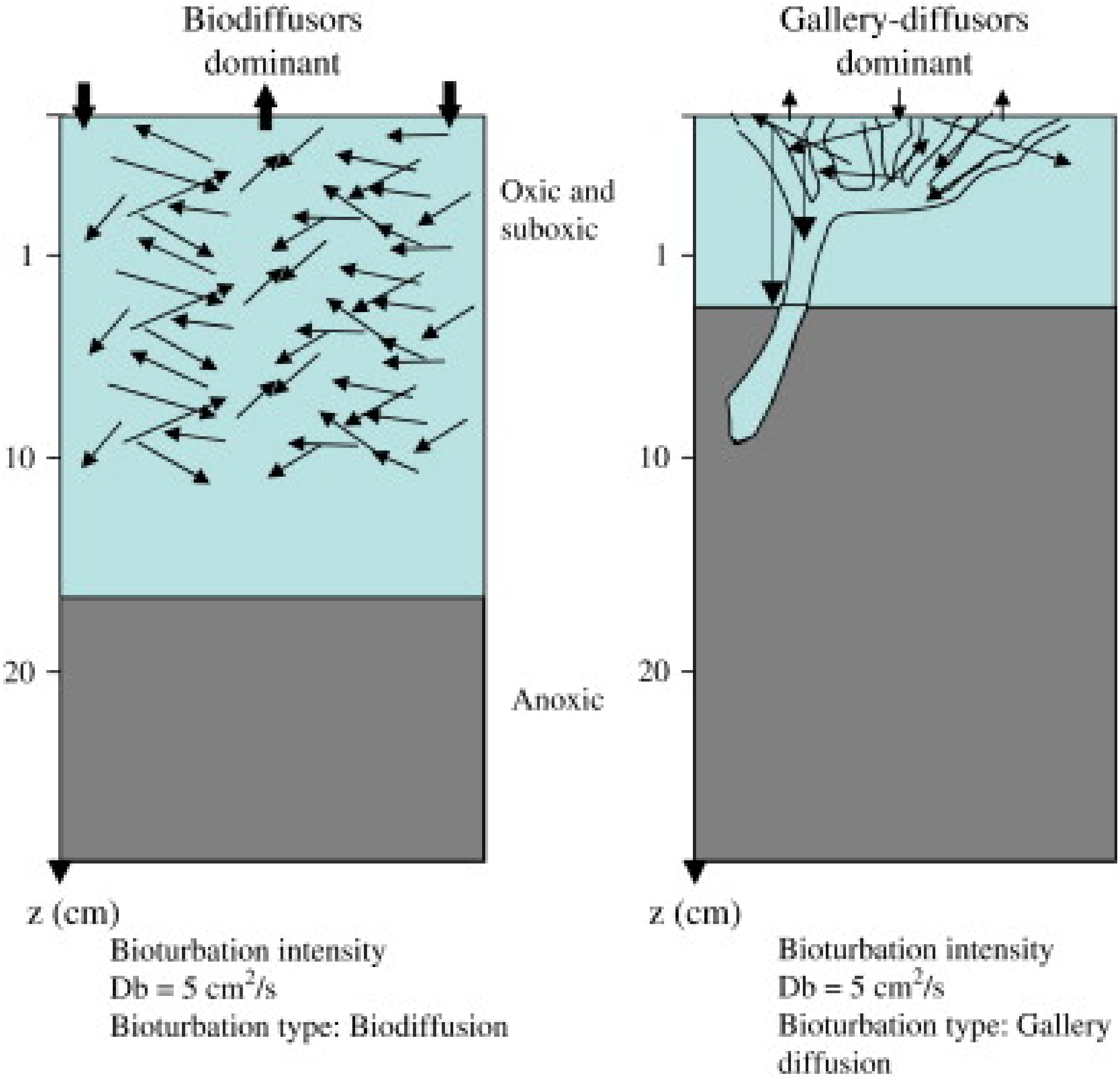

Fig. 3: Schematic diagram showing the type of bioturbation organisms encountered in the sediments of the Thau lagoon. Biodiffusors dominate at the central site (C4) whereas gallery diffusor dominate at the organically enriched site.