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Editorial

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

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 redox and biogenic elements, such as C, O, P, S, Si, Fe, and Mn (Middelburg and Soetaert, 2004). Coupled together with the sources (rivers, water table, surface runoff, and 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. The microbial and phytobenthic activities taking place in surface sediments promote changes in oxidation state of porewaters and sediment, in porewater pH and in reduced chemical species. This 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: (1) early diagenetic processes, which generate the chemical conditions of the environment; (2) processes leading to the transfer of contaminants from particles toward biofilms, water column, and organisms; and (3) 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 km^2, 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 *Crassostrea 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 m in diameter and is at a depth of 8 m. 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: December 2001 and January 2002; M2: April 2002; M3: August 2002; M4: January 2003; and M5: May 2003).

2.2. Overview of the early diagenetic processes

A combination of techniques was used to obtain an overall view of early diagenetic processes at the two main stations. Porewater extraction from sediment cores and in situ

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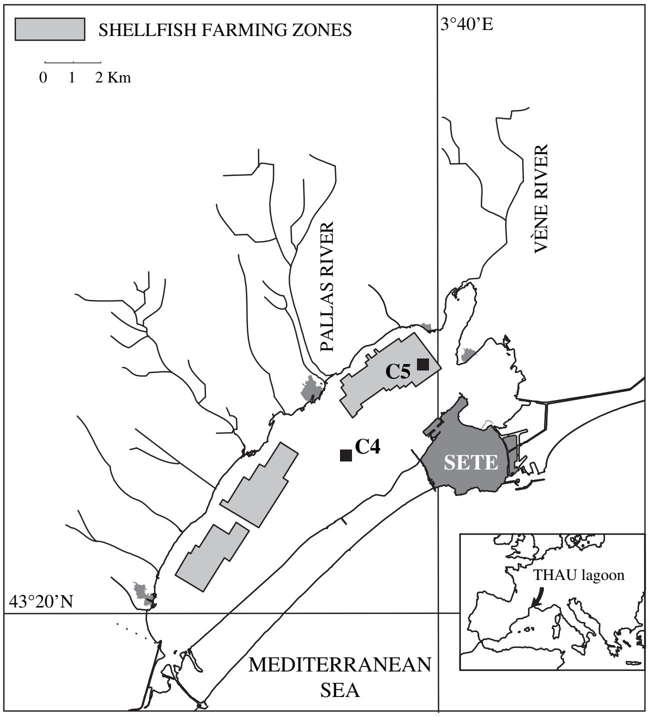

Fig. 1. Sampling site and locations of the two stations in the Thau lagoon (station C4 in the central part of the lagoon and station C5 near the shellfish farming area).

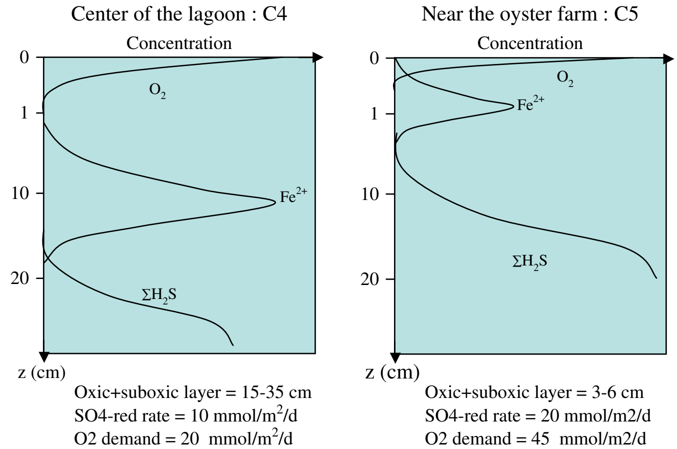

Fig. 2. A schematic view of early diagenesis at the two sites studied in the Thau lagoon. Organic matter recycling is enhanced in the sediments of the oyster farm leading to reduced conditions close to the sediment–water interface.

porewater 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, and calcium), minor cations (lithium, strontium, and barium), redox sensitive species (dissolved manganese, ferrous iron, sulphate, sulphide, ammonium, and nitrate) and other diagenetic parameters (pH, alkalinity, soluble reactive phosphorous, and 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 centre 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 led 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 1–2 mm, Dedieu et al.) one. 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 a 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 15–35 cm 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 cm. 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 microniches 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 variabilities 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 Q_{10} 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 1 μM) 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 the 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, and Co). They exhibited a significant correlation with Mn fluxes (Point et al.) which can be used as a proxy for such suboxic to anoxic remobilization 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 displays 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.

Table 1
Average trace metal fluxes in the two diagenetic contexts in April 2002 (Hg species data are from May 2003, see Point et al.). 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	Centre 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

Indeed, processes dominating uranium behaviour are linked to sulphate reduction which acts as a sink for uranium by reducing the U-oxides 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 mobilization. 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 methylmercury 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 20−100 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 methylmercury formation as influenced by both benthic and pelagic dynamics (Monperrus et al.), which explains the lack of relationship between methylmercury and Mn fluxes.

The intensity of benthic remobilization 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 bioturbation 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 sites 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 (Fig. 3). 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 a 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.

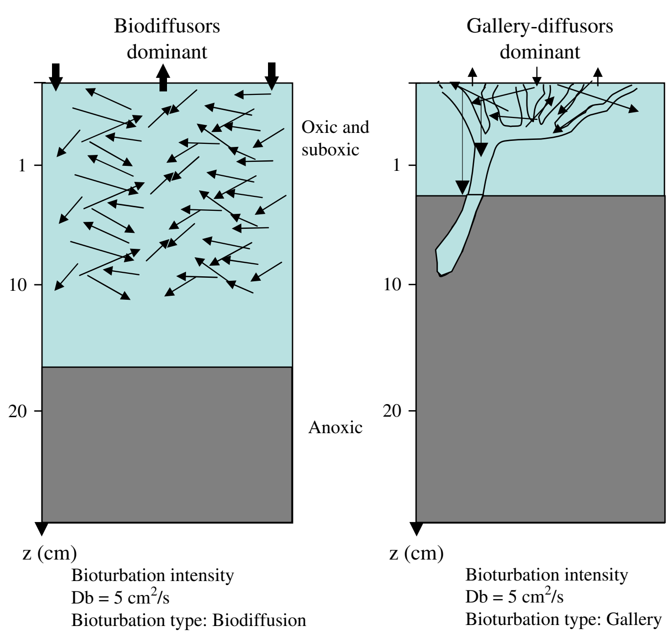

Fig. 3. Schematic diagram showing the type of bioturbation organisms encountered in the sediments of the Thau lagoon. Biodiffusors dominate at the central site (C4) whereas gallery-diffusors dominate at the organically enriched site.

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 luminophore-D_b. 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 oxyhydroxides, the concentration of free sulphide partly controlled by reduced iron, the availability of organic substrates, and the intensity of bioturbation and irrigation. Thus temporal and spatial variations of biogeochemical cycling of elements such as C, O, Fe, and 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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List of papers in this special issue

Diagenesis

Anschutz, P., Chaillou, G., Lecroart, P. Phosphorus diagenesis in sediment of the Thau Lagoon.

Dedieu, K., Rabouille, C., Thouzeau, G., Jean, F., Chauvaud, L., Clavier, J., Mesnage, V., Ogier, S. Benthic O_2 distribution and dynamics in a Mediterranean lagoon: an in-situ microelectrode study.

Jézéquel, D., Brayner, R., Metzger, E., Viollier, E., Prévot, F., Fiévet, F. Two-dimensional determination of dissolved iron and sulfur species in marine sediment, pore-waters by thin-films based imaging. Thau lagoon (France).

Metzger, E., Simonucci, C., Jézéquel, D., Viollier, E., Sarazin, G., Prévot, F. Benthic response to shellfish farming in Thau lagoon: pore water signature.

Thouzeau, G., Grall, J., Clavier, J., Chauvaud, L., Jean, F., Leynaert, A., Longphuirt, S., Amice, E., Amouroux, D. Spatial and temporal variability of benthic biogeochemical fluxes associated with macrophytic and macrofaunal distributions in the Thau lagoon (France).

Metal mobility and fluxes

Amiard, J.-C., Geffrard, A., Amiard-triquet, C., Crouzet, C. Relationship between the lability of sediment-bound metals (Cd, Cu, Zn), and their bioaccumulation in benthic invertebrates.

Metzger, E., Jézéquel, D., Elbaz-Poulichet, F., Simonucci, C., Viollier, E., Sarazin, G., Seidel, J.-L., Prévot, F. Influence of diagenetic processes in Thau lagoon on cadmium behavior and benthic fluxes.

Monperrus, M., Tessier, E., Point, D., Vidimova, K., Amouroux, D., Guyoneaud, R., Leynaert, A., Grall, J., Chauvaud, L., Thouzeau, G., Donard, O.F.X. The biogeochemistry of mercury at the sediment water interface in the Thau lagoon. 2. Evaluation of mercury methylation potential in both surface sediment and the water column.

Muresan, B., Cossa, D., Jézéquel, D., Prévot, F., Kerbellec, S. The biogeochemistry of mercury at the sediment water interface in the Thau lagoon, 1. Partition and speciation.

Point, D., Monperrus, M., Tessier, E., Amouroux, D., Chauvaud, L., Thouzeau, G., Jean, F., Amice, E., Grall, J., Leynaert, A., Clavier, J., Donard, O.F.X. Biological control of trace metal and organometal benthic fluxes in a eutrophic lagoon (Etang de Thau, Mediterranean sea, France).

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Schmidt, S., Jouanneau, J.-M., Weber, O., Lecroart, P., Radakovitch, O., Gilbert, F., Jézéquel, D. Sedimentary processes in the Thau Lagoon (South France): from seasonal to century time scales.

References

Emerson, S., Hedges, J., 2003. Sediment diagenesis and benthic fluxes. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry. Elsevier–Pergamon, Oxford, pp. 293–319.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern Atlantic: suboxic diagenesis. Geochimica et Cosmochimica Acta 43, 1075–1090.

Lotze, H.K., Lenihan, H.S., Bourque, B.J., Bradbury, R.H., Cooke, R.G., Kay, M.C., Kidwell, S.M., Kirby, M.X., Peterson, C.H., Jackson, J.B.C., 2006. Depletion, degradation and recovery potential of estuaries and coastal seas. Science 312, 1806–1809.

Middelburg, J.J., Soetaert, K., 2004. The role of sediments in shelf ecosystem dynamics. In: Robinson, A.R., McCarthy, J., Rothschild, B.J. (Eds.), The Global Coastal Ocean Multiscale Interdisciplinary Processes. The Sea, vol. 13. Harvard University Press, pp. 353–373.

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