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Chapter 1

BIOGEOCHEMISTRY STUDY IN MANGROVE ECOSYSTEM SEDIMENTS USING DIALYSIS POREWATER SAMPLER

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Abstract

This chapter deals with the biogeochemistry of sediment in coastal ecosystem as mangrove and detailed the dialysis porewater sampler in order to evaluate nutrients

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fluxes at the sediment-water interface. The chapter is structured in three different part :

(i) Several porewater techniques are detailed and their advantages-disadvantages are discussed. Conventional methods of porewater sampling such as centrifugation or squeezing, present some limitations that is an over-estimation of dissolved substances owing to the highest pressure imposed to the sediment. Then other sampler designs (DET, Dialyser), with a dialysis membrane insert into the sediment, waiting for its equilibration without sediment coring are discussed. They allow to obtain continuous profiles of the sediment-water interface with high vertical resolution.

(ii) The dialysis technique (type Hesslein) is described and adapted for mangrove sediments (Somone, Senegal). Its provides concentration gradient of nutrients, useful to quantify the nutrients fluxes released from sediment compartment. However, this technique required an equilibration time, which has been determine with an *in situ* experiment, detailed in the chapter.

(iii) The equilibration time has been also determine with a numerical model of diffusion. The principle, sensibility tests and physical parameters of the diffusion model, are detailed. Furthermore, the diffusion model is calibrated with real data sets in order to fit the model.

1. Introduction

Coastal areas as lagoons, estuaries, deltas, received runoff waters and suspended solids from the watershed. Indeed, these nutrient inputs constitute the basis of primary production and food webs of the coastal ecosystems (Odum and Heald,1975; Day *et al*., 1996 ; Pasco and Baltz, 2011). But nowadays, the nutrient inputs are often in excess, leading the coastal ecosystems to eutrophication, manifested by excessive development of vegetation resulting to anoxic conditions and production of toxic phytoplankton (Sousa and Dangremond, 2011).

The nutrients are not only coming from the watersheds runoff but also from the sediment, internal nutrients source. Previous studies have established that the sediment compartment is an important sink for nutrients, especially for phosphorus (Boström *et al*., 1988) and contains much higher concentrations than the water column (Xu *et al*., 2012). This compartment could also become a source through the release of dissolved species under well defined pH and oxydo-reduction conditions as well as hydrodynamics conditions (Böers, 1991; Song and Müller, 1999; Bally *et al*., 2004). Indeed, studies of water quality in coastal mangroves must integrate the geochemistry of the sediment compartment and especially quantified the nutrients fluxes at the sediment-water interface.

In this context, sampling the porewater is the first step to quantify nutrients concentration gradients in order to estimate nutrient fluxes at the sediment-water interface. Some techniques can track very fast biogeochemical processes in the sediment sub-surface and are concerned with instantaneous changes related to physical forcing as the tide or instaneous events in suspension/erosion (Guédron *et al*., 2012; Xu *et al*., 2012). Others techniques can integrate measurements over longer time scales of one to several weeks (Hesslein, 1976; Bally *et al*., 2005; Mesnage *et al*., 2007). Among these techniques, the dialysis porewater sampler (Hesslein, 1976) is now well developed. It is adapted for measuring water quality in aquatic ecosystems, especially in the evaluation of nutrients (NO_2^-, NO_3^-, NH_4^+,

PO_4^{3-}) (Bally *et al*., 2005; Mesnage *et al*., 2007; Mesnage *et al*., 2013) metals or trace elements (As, Co, Cr, Hg, ...) (Rigaud *et al*., 2013).

The conventional methods of porewater sampling such as centrifugation or squeezing present some limitations that is an over-estimation of dissolved substances owing to the highest pressure imposed to the sediment. Then, the advantage of the dialysis sampler is to insert the dialysis design into the sediment, waiting for its equilibration without sediment coring. It allows to obtain continuous profiles of the sediment-water interface to a depth of 40 cm, providing sufficient porewater volume for all chemical species studied. Furthermore, the gradient of nutrients concentration obtained is useful to estimate the nutrients fluxes and to quantify the nutrients release from sediment compartment. However, this technique required an equilibration time which varies according to the sediment characteristics and climatic domain. In fact, this limit of the sampler, is useful when studying intertidal ecosystems, because it takes into account the natural variability of the environment by integrating several tidal cycles. Moreover, the dialyser technique is well adapted for estimation of potential nutrients fluxes by considering the concentration gradients over 40 cm depth sediment.

As a consequence of the variable equilibration times given in the literature, it is useful to determine a site specific equilibration time based on *in situ* experiment in the Somone mangrove sediment (Senegal). The *in situ* sampling strategy has consisted of eight peepers inserted all together at the same initial time and sampled after 11, 18, 19 and 20 days. Anions and cations profiles are compared with references profiles obtained by a coring-centrifugation method in order to determine an optimum equilibration time (Sakho, 2011). Furthermore a physical diffusion model has been used to estimate an ex-situ optimal equilibration time (Mesnage *et al*., 2013)

The aim of this chapter is to present (i) an overview of the advantages-disadvantages of the porewater extraction methods; (ii) the principle of the dialysis porewater sampler and especially its application in mangrove sediments, (iii) a recent development of the dialysis porewater sampler by using a physical diffusion model to optimize the dialysis equilibration time.

2. Methods of porewater sampling : an overview

A distinction can be made between methods that sample from which porewater can sampled in the laboratory, and *in situ* samplers.

2.1. Methods in laboratory with sediment coring

Centrifugation and squeezing methods required a first step in the field indeed sediment is sampled using corers pushed into the sediment, closed and transported to the laboratory. Then, the sediment is cut into slices and centrifuged and/or squeezed.
Although this low-cost method is very easy to realise it has several disadvantages : that is (i) oxidation of sediment interface may occur, (ii) temperature and pressures modifications, (iii) over-estimation of dissolved substances ions concentration by desorption of sorbed ions (phosphate) during the centrifugation.

These methods whose imposed physical pressure on the sediment lead to an over-estimation of dissolved substances.

2.2. In situ sampling of interstitial water

2.2.1. benthic chambers

The technique of benthic chamber consists of a transparent metacrylate hemisphere attached to PVC rings inserting into the sediments by divers. These benthic chambers cover an area from 0.1 to 0.2 m^2 with a total water volume from 5 to 40 litres depending on the design chosen (Hopkinson, 1987; Mazouni *et al*., 1996, Berelson *et al*., 2003).
The water volume of the chamber is stirred to prevent stratification inside of the water chamber. A Teflon valve fixed on the side of the chamber allowed the water sampling, by divers, using a syringe. Then after filtration, chemical analyses are performed on these water samples.

The frequency of water sampling varying from one to several hours depending of the authors, during the incubation time from 24 to 48 hours. Furthermore, nutrients fluxes can be estimated as the slope of linear regression between concentration of the solute and the incubation time (Berelson *et al*., 2003)

This method is especially used to estimate benthic oxygen and nutrients fluxes at the sediment-water interface (Lehman *et al*., 2004; Berelson et al. 2003) and in the modelling of primary production (Chapelle *et al*., 2000).

2.2.2. DET (Diffusional Equilibration in Thin-films) and DGT (Diffusional Gradient in Thin-films)

The principle of the technique DGT and DET is based on Ficks first law of diffusion (Zhang H. and Davison W., 1995; Zhang *et al*., 1999). The technique of the diffusive Gradient in Thin films (DGT) appears superficially similar to DET, but it separates species kinetically different (Davison *et al*., 2000).

The diffusive equilibrium is reached between porewaters ions and in a thin film of gel of thickness < 1 mm (Davison *et al*., 1994; Xu *et al*., 2012). The DET-DGT techniques have been developed and used for *in situ* measuring labile species in marine and freshwater (Davison W. and Zhang H. 1994; Zhang *et al*., 1995; Krom *et al*., 1994; Fones *et al*., 2001) and even in rivers ecosystems (Gao et al. 2007, Leermakers *et al*., 2005). It provides an *in situ* measuring labile species in aqueous systems especially for traces metal.

DET/DGT design are initially inserted into sediment, placed by hand for shallow waters But these techniques can also be used in deeper waters using scuba divers. After deployment, the resin gel layers are sliced and eluted with acid, metals can be analysed by absorption spectroscopy (AAS) or inductively coupled plasma absorption spectrometry (ICP-MS).

2.3. Dialysis porewater sampler

2.3.1. Dialysis principle

The dialysis porewater sampler is one of the first diffusion method described for sampling water in lake sediments (Hesslein, 1976).

The principle of equilibration is the ion diffusion across a membrane until equilibrium between the porewater and the sampler cell (Figure 1).

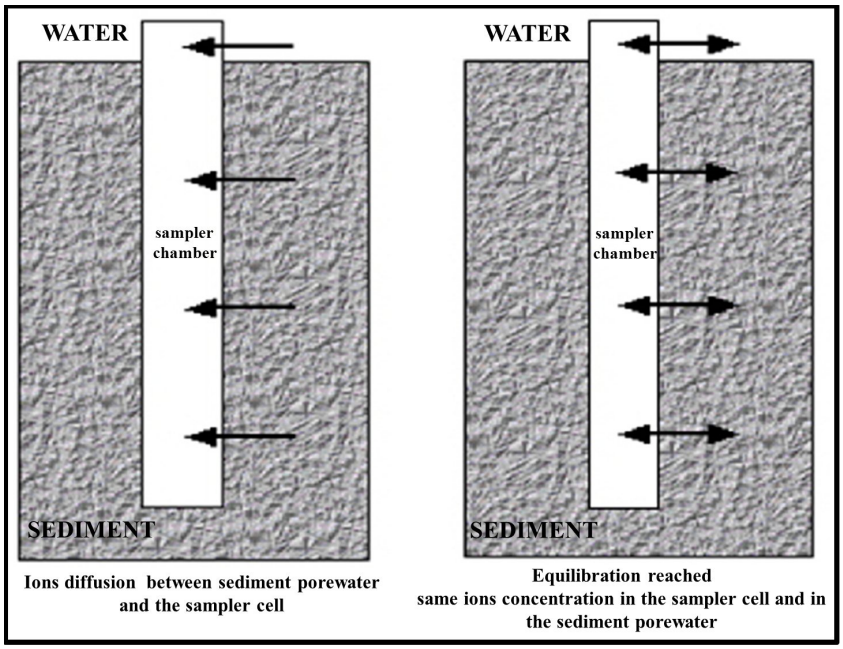

Figure 1. Principle of the porewater sampler

Nutrients or trace metals solutes concentrations are obtained and permit the fluxes calculation according to the first Ficks law Eq. (1) , modified for sediment (Figure 1). The flux is given by the modified Ficks law:

$$J_i = -\phi.D.\frac{dc_i}{dx} \qquad \text{in mmol} \times \text{m}^{-2} \times \text{j}^{-1} \tag{1}$$

where ϕ is the porosity of sediment, D diffusion coefficient of the ion into water, and dc_i/dx the gradient of concentration of solute i. The porosity (or tortuosity) increase the distance an ion needs to travel between the surrounding sediment and the sampler chamber.

2.3.2. Dialysis design and preparation

The porewater sampler design, type Hesslein (Hesslein, 1976), consists of a $51.5 \times 22 \times 3$ cm plexiglas sheet in which fixed volume chambers ($5.6\ \text{cm}^3$) are spaced 1 cm. Each dialysis sampler has two series of 40 cells, these are filled with deionised water purged by N_2 bubbling then covered with an inert polysulfone membrane of 0.2 μm porosity (Millipore, Durapore), sealed with screws each centimetre and overlain by a plexiglass sheet with apertures matching the cells.

The equilibration time required for the diffusion sampler is around 3 weeks (Bally *et al.*, 2005), this time may depend on physical characteristics of the sediment (porosity, temperature, ...). Pore water samples are removed using plastic syringes. The samples acidified with

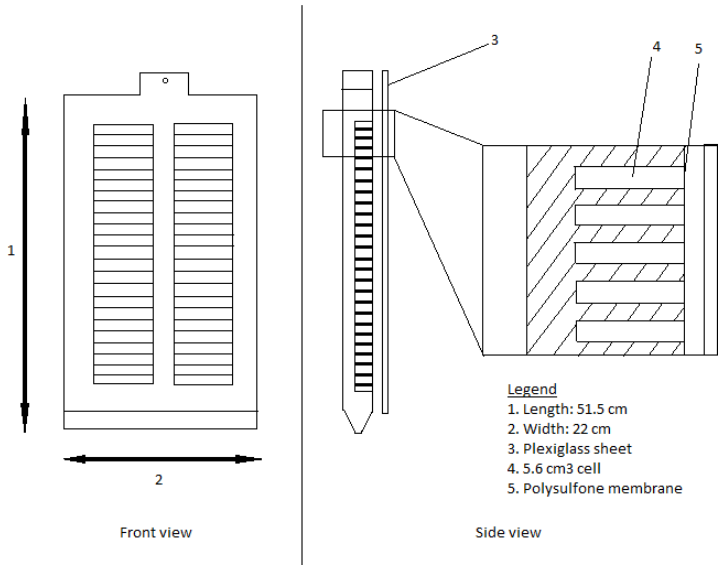

Figure 2. The porewater design, Hesslein type

HCl and stored in conditioned 5 ml haemolysis tubes are frozen until analysis of dissolved species.

2.3.3. Dialysis deployment

Figure 3. Deployment, insertion into sediment, Somone estuarine ecosystem (Senegal). Photographs made by V. Mesnage.

The samplers are insert, at low tide, vertically into the sediment leaving 6 or 7 chambers above the sediment surface and 34 or 33 below.

The dialysis technique is widely used to estimate nutrients fluxes in lakes, or marine environments (Serbst *et al*., 2003; Albéric *et al*., 2000) as well as lagoons, shallow waters or coastal wetlands (Jézéquel *et al*., 2007; Man *et al*., 2004). It is easy to deploy into sediment and allows a lot of replicates. This latter characteristic is particularly appreciated when study focuses on heterogeneous substrates as intertidal sediments.

In lakes or lagoons, the time necessary to reach the equilibration is one the limit of the

Figure 4. (left) Removal of the dialyser after 20 days equilibration in the sediment, (centre) Porewater sampling using syringes, probes are stored in acidified tubes, (right) ions concentration gradient determination over the depth. Photographs made by V. Mesnage.

dialysis technique. In contrast in intertidal ecosystems, this time allows to take into account the natural variability of the environment by integrating several tidal cycles. Moreover, the dialysis technique is well adapted for estimation of potential nutrients fluxes by considering the concentration gradients over 30 cm depth sediment.

This technique permits to sample interstitial waters with little or no change in temperature or pressure especially adapted when analysis of gas is required. The sufficient porewater volume sampled is suitable for all geochemical analysis.

As well, depending of the aim of the study, modelling of primary production or diagenesis process in sediment, the choice of the method will be the benthic chambers or the dialysis sampling technique.

The DET-DGT, *in situ* diffusional techniques for porewater sampling, are quite similar than dialysis method but the sampling medium is a hydrogel rather than a solution retained by a dialysis membrane. They are both adapted to calculate nutrients or trace metal fluxes at the sediment-water interface. The main difference between dialysis and DET/DGT technique is the equilibration time needed for these methods and the spatial resolution. Indeed a millimetre spatial resolution for DET-DGT methods against a range of centimetre spatial resolution for the dialysis classical technique.

2.4. Advantages and limitations of each methods

Methods	Advantages	Limitations
Centrifugation method and Squeezing method	• Providing informations on both bulk sediment and pore-water at the same sediment sampling station • Easy to deployed , lots of replicates can be made • Not expensive materials	• Modification of the sediment pressure conditions • Over-estimation of dissolved substances by desorption the solutes (especially for phosphate)
Benthic chambers	• Fluxes at the sediment-water interface with a short time-scale • Easy to deployed in shallow waters (lagoons) and/or estuaries environment	• Estimation of benthic fluxes, only at the sediment interface, adapted for the study of primary production • The sediment depth is not taken into account • Estimation of instantaneous nutrients fluxes • No idea of the diagenesis process over the sediment column • Expensive material • Dyvers are needed for water sampling in the chamber during the incubation time
DET DGT	• Very short equilibration time • High resolution over the depth (millimetre) • Small dimension of the designs, high reproducibility • Easy to deploy in sediments	• Gels are very thin also easily damage • Have to be handle with care, also difficult to use in the field especially in tropical estuaries • Very small volume of interstitial water sampled. limiting the number of chemical analyses, except in the case of analyses on a ICP-MS • Expensive material

Methods	Advantages	Limitations
Dialysis porewater sampler (Peepers)	• Continuous ions profile between sediment and water column • Sampling profiles in continuous the water column and the sediment. That is the sediment-water interface • Minimal disturbance of sediment-water interface • Estimation of potential nutrients fluxes by integration of the concentration nutrients gradients over 30-40 cm depth sediment. • Lots of replicates • Easy to deployed into sediment- (easy to used) • Little or no change in temperature or pressure especially when analysis of gas is required • Adapted for shallow waters and intertidal ecosystems by integration of several tidal cycles • Sufficient porewater volume samplers (1 to 20 ml depending on the dialyser design)	• Relatively expansive : dialyser manufacturing and membrane cost • Can be used several times in the field. Hard-wearing apparatus • Choice into material used for dialyser-sampler, take care in ions precipitation (especially for trace metals analyses) • Choice of the membrane (thin and polysulfone) • Oxygen contamination of dialyser cells (in the case of anoxic sediment) • Time equilibration of the sampler (two weeks) • Scuba divers needed for deployment if water column deeper than 1 meter

Table 1. Advantages and limitations of porewater techniques

2.5. Application to mangrove sediments : The Somone estuary

2.5.1. Characteristics of the Somone watershed and estuary

Located at the Petite Côte of Senegal (14^o290N and 17^o050W) at 70 km south of Dakar, Somone is a small coastal river that flows into the Atlantic Ocean by a microtidal lagoonal-estuarine ecosystem. Its watershed covers an area of 420 km^2 and is located in the Sahelo-Soudanian climatic zone.

The monsoonal flux, originating from the Sainte-Hélène anticyclone in the south Atlantic, controls the rainy season in Senegal, which lasts from June to October.

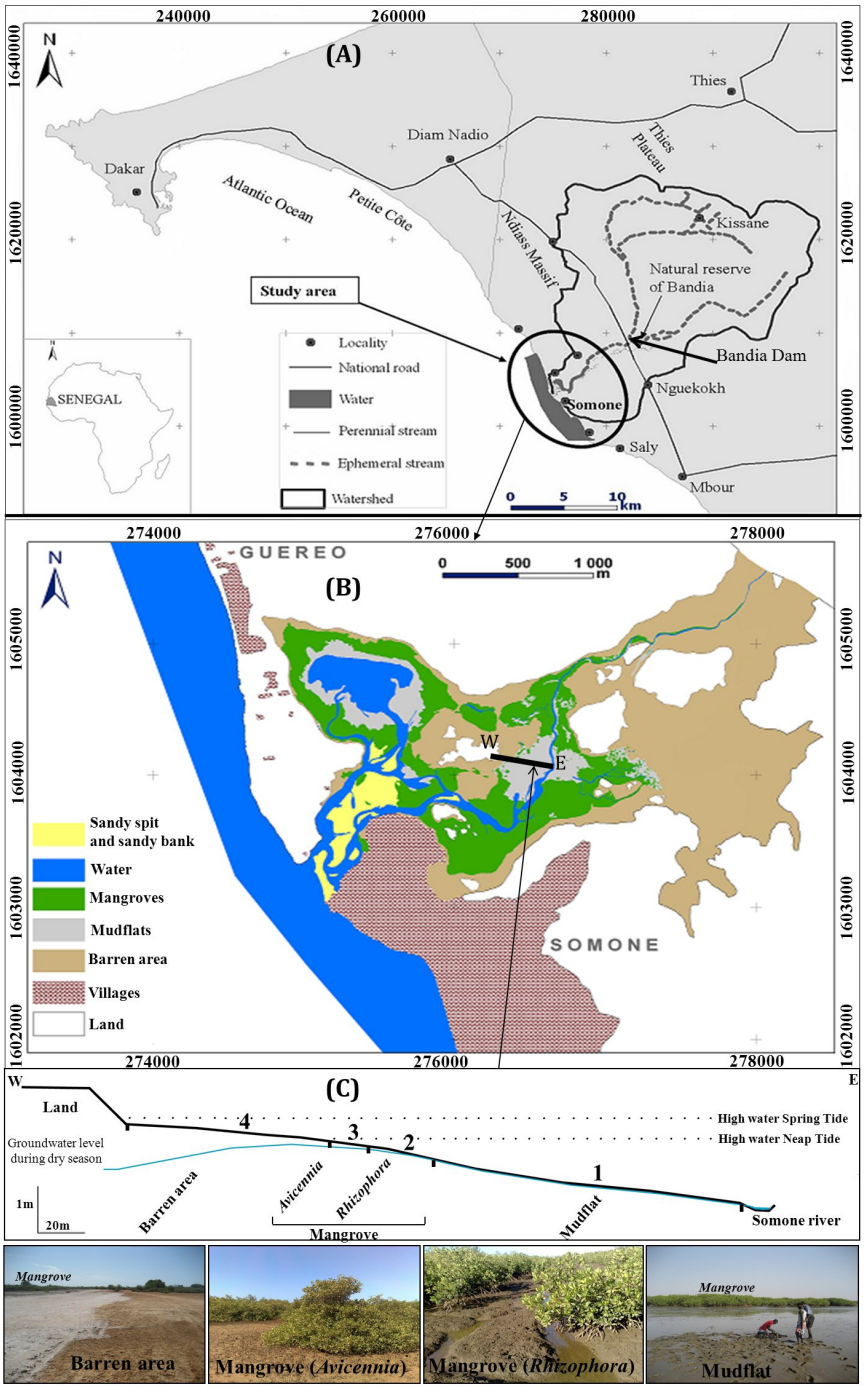

Figure 5. Study site. **A**: location of the Petite Côte of Senegal; **B**: estuary and lagoon; **C**: cross-section of the geomorphological units of the Somone estuary; bottom : profile photographies corresponding to the points indicated on the above cross-section.

The dry season is longer, usually about 7 months (November to May), with temperatures ranging from 23° C to 32° C.

The hydrologic network of the Somone system has little hierarchical organization. It is formed by the confluence of two ephemeral streams (Fig. 5 (top)) that drain the Thies Plateau, part of the Ndiass horst, and the sandy plain. The stream draining the eastern part is 30 km long, and that draining the western part is 20 km long. The Bandia reserve is located at their confluence (Fig.5).

Most of the flow occurs in August and September, coinciding with maximum precipitation. Discharge data, although discontinuous, indicate that the maximum discharge does not exceed 10 $\mathrm{m}^3.\mathrm{s}^{-1}$ during the wet season.

The lagoonal-estuarine ecosystem of Somone covers an area of 7 km^2 in the downstream zone of the watershed (Fig. 5). This ecosystem is mainly influenced by marine inputs and is characterized by an inverse salinity gradient. It can be divided into three parts: the estuary to the east, the lagoon to the north, and the estuary mouth to the west (Fig. 5 (top-middle)).

Three morphological units are present in the Somone Estuary. The first is the mangrove forest (Fig. 5 bottom), which is characterized by it morphological and physiological adaptation to the constrained environmental requirements (e.g. the hydromorphology and periodic flooding). These adaptations include aerially exposed roots, pneumatophores and salt-secreting glands, which permit them to survive in an anaerobic and unstable environment.

The second morphological unit is the mudflat (Fig. 5 bottom), which corresponds to deforested mangrove areas and is composed mainly of fine-grained sediments (mean-size < 63 mm). These two morphological units are in the intertidal zone, which is submerged at high tide (Fig. 5 bottom).

The third morphological unit is the barren area (Fig. 5 bottom), which designates a hypersaline zone, devoid of vegetation, which is submerged by extremely high tides, and which undergoes an annual alternation of flooding and desiccation (Marius, 1985).

Evapo-transpiration is intense and the soil water content is low. The soil is sandy, acidic (pH < 7 at the subsurface sediment and pH < 6.5 at 5 cm under the surface sediment), and saline (70 PSU). The formation of efflorescence prevents the establishment of vegetation (Fig. 5 bottom).

This morphological unit is common in Senegal and in the literature its presence identifies degraded mangrove forest (Lebigre and Marius, 1985; Diop, 1990; Kaly, 2001).

With progression from the Somone River to the land (i.e., from the intertidal to the supratidal zone), one encounters first the mudflat, then the mangrove forest and finally the barren area (Fig. 5 (bottom)). A sand spit (Fig. 5 B) is located at the estuary mouth and extends for 400 m to the north. It protects the sand banks from wave and swell induced erosion.

The lagoon (Fig. 5) is the largest water reservoir of the ecosystem and tidal fluctuation is dependent on the maintenance of the marine inlet through the tidal channels (Fig. 2). The geomorphology of the Somone Estuary and its watershed have been subject to anthropogenic modifications, including the building of several dams upstream in the Somone River (the Bandia and Kissane Dams, Fig. 5, which were constructed to provide drinking water for wildlife in the Bandia Reserve), sand quarrying in the 1990s and basin modifica-

tion for industrial oyster cultivation. The hydrological circulation has also been perturbed downstream of the Somone river.

The average rate of sedimentation of mud flats is very low, 2 mm.an-1. The total organic carbon in sediments is also low, $< 4\%$ and reflects the low production of mangrove organic matter because it is a young mangrove and stunted form. Diagenetic processes are anaerobic and mainly in the top 10 cm of the sediment, on the recent deposit.

2.5.2. In situ sampling strategy, equilibration experiments

Based on previous work on the Seine estuary (Bally *et al*., 2004) and the Thau lagoon (Mesnage *et al*., 2007), we chose a strategy to implement 7 peepers on the Somone mudflat at the same date (05 August 2008) and then sampled it after 11, 18, 19 and 20 days respectively.

We also sampled a sediment core at 05 August 2008 in order to obtain a *reference profile concentration* of each element.

The interstitial water were sampled *in situ* to avoid O_2 exchange and were immediately placed into haemostatic vials previously filled with 20μl concentrated HCl to prevent co-precipitation of phosphate with $FeOOH$, for example (Bally *et al*., 2004).

The porewater samples were transported to the laboratory at 4° C and stored at -18° C until irons and nutrients were analysed. Then, in order to determine the equilibration time of dialysis, we compare, for each element, the *reference profile* to those obtained at 11, 18, 19 and 20 days. The optimal equilibration time is assumed to be reached when one of these profiles is superimposed to the *reference profile*.

2.5.3. Nutrients porewater geochemistry

The concentration profiles of porewater in sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-) and sulphate (SO_4^{2-}), shown in Figure 6, are those of the test equilibration of dialysis on the intertidal mudflat of the estuary Somone. Each graph (from *A* to *F*) shows a change in the concentration depending on the depth of all the elements Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} respectively at the four equilibration test dates : 11, 18, 19, and 20 days, respectively denoted in the legend T11 , T18, T19 and T20 (Figure 6).

Profiles in black color, denoted T0 in the legend, represents the variation according to the depth of the concentration of chemical elements and corresponds to the reference profile. These references profiles obtained by coring the sediment exhibit systematically slightly higher values than the *in situ* values; this behaviour is in accordance with one of the disadvantages of the coring method discussed above.

Whatever the ion considered (cations or anions), it appears that the shape of the profiles according to depth have two distinct forms: (i) from 0 to 10 cm below the sediment surface, where variations between equilibration time is very important, (ii) a deep level (10-33 cm) characterized by lower temporal variations (Figure 6). Thus, under the analysis of various elements (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}), we find that profiles at 11 days are the most similar to those concentrations profiles of the core reference but only between 0 and -10 cm depth about. The highlight is the sharp decrease in concentrations observed in profiles 18, 19 and 20 days between 0 and -10 cm depth. It could be due to the dilution of porewater by rainwater following the rainfall from the 14th to 16th days.

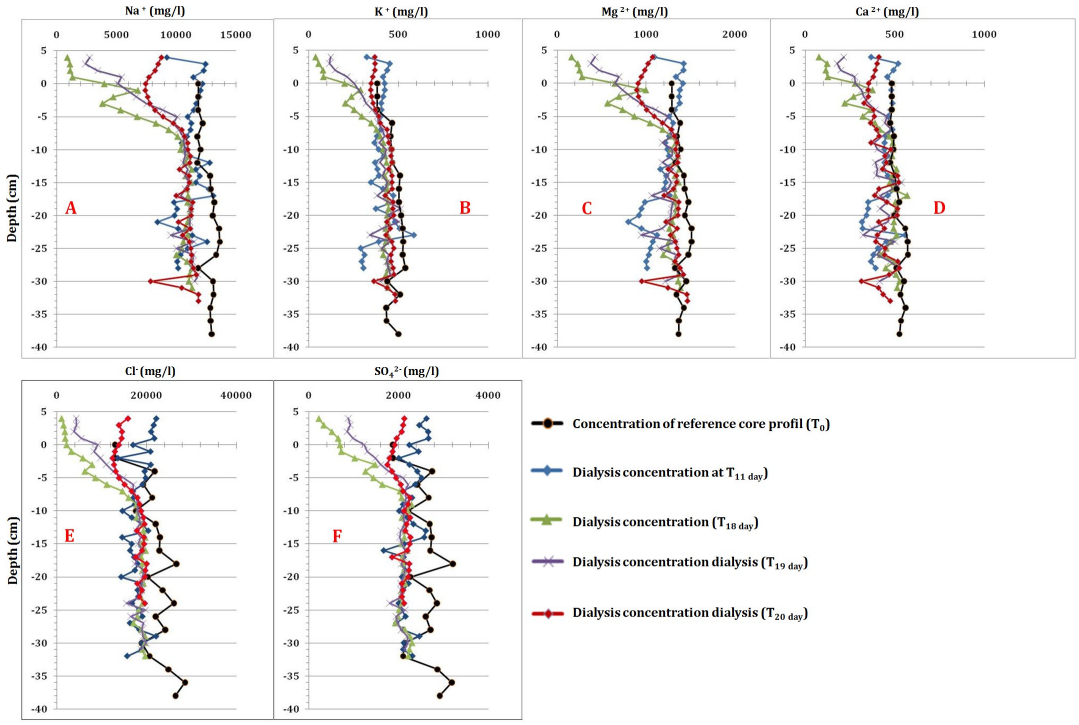

Figure 6. Equilibration dialysis tests for various elements (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}. The *reference profile* is the one obtained by coring sediments.

Thus, we note that for all chemical elements equilibration time seems effective in 11 days, but only for the top 10 cm of sediment (Fig. 6). The decrease in concentrations 18, 19 and 20 days observed between 0 and -10 cm depth, shows that the intertidal mudflat is very responsive to rainfall inputs. The first 10 cm of sediment the mudflat are recent deposits (Sakho *et al*., 2011) and ion exchange will seem larger. In depth (-10 to -33 cm), equilibration seems to require a longer time. Most often at the depth, this is the profile to 20 days which is closest to the reference profile (Fig. 6). These deposits below 10 cm depth are the sediments of the former mangrove mudflat observed between 1946 and 1954 (Sakho *et al*., 2011). They had to undergo major phenomena of compaction which therefore could slow ion exchange and therefore equilibration. Following the analysis of the profiles of different chemical elements, we will retain an optimal equilibration time of 11 days for the first 10 cm of sediment. This time is much shorter than the 23 days set by Bally (Bally *et al*., 2004) for estuaries in temperate environments. Specific estuaries in dry tropical coastal setting, characterize by a very contrasting seasons, environmental factors (temperature, salinity) seem to explain the importance of biogeochemical reactions.

3. Recent development of the dialysis porewater sampler

3.1. Physical diffusion model : principles and limitations

3.1.1. Transport Equation in a Sediment Layer

A "diffusive-flux-between-two-compartments" numerical model has been developed in order to calculate the solutes concentration between the peeper's chamber and the surrounding water (i.e. porewater) inside of a wet sediment. Thereby, the numerical model computed in two successive steps : (i) the diffusive flux within the sediment; (ii) the same diffusive flux but through the peeper membrane. Thus, the model is described as a two compartments model: (i) the dialysis chamber and (ii) the sediment (i.e. porewater) with a flux condition at the interface (the peeper membrane).

The model, based on the development of the Cauchy condition within the membrane (affine relationship between the flux diffusive density of the component and the mass force), considered the following assumptions :

- the problem is treated as a 1-dimensional one, that is diffusion occurs only along the horizontal direction. This assumption will be validated later by the estimate of the gradient of concentration along the vertical direction.

- no-convection will be considered in the analysis; the Péclet number is assumed to be very small, and only diffusion of the major elements is considered.

- the solutes concentration within the sediment is constant, so the re-load by the solid phase of the sediment has been taken into account in the modeling. This means that in the far field (far from the dialyser), an uniform porewater concentration is considered.

- the boundary between the two porous media are constitute by a polysulfone membrane which no accumulate solute, and its thickness negligible, has not been take into account in the modeling.

- in the porous media, due to the presence of particles of different sizes and orientation, the diffusivity is lowered in comparison to the one in homogeneous fluid. An effective diffusivity is then used, this one takes into account a random distribution of pores in the heterogeneous media.

We define the *outside* domain Ω_1 as the porous medium and the *inside* one Ω_2 the cell of the dialyser. Both domains are separated by a membrane which allows transfer of ions on both sides.

One-dimensional diffusion problem in porous medium (unsteady transport in the fluid phase), when mass transport takes place in the direction of x-axis, can be described by the following time dependent differential equation :

$$\frac{\partial c_1}{\partial t} = -\frac{\partial}{\partial x} J_c \tag{2}$$

where J_c is the diffusion flux, c_1 is the solute concentration in the outside domain Ω_1 and t is the time. In the case of Fickian diffusion given previously by Eq. (1)

$$J_c = -D^{eff}\frac{\partial c_1}{\partial x} \tag{3}$$

where D^{eff} is the "effective" diffusivity tensor of the solute in the bulk sediment, dependent upon the system's temperature, pressure and composition (Welty *et al.*, 1969) and is constant under the assumption that these parameters remain unchanged with time. Because of the linearity of Ficks first law the size of the domain has no influence on the effective diffusion coefficient (at the macro-scale), and the effective diffusion coefficient is only a function of the pore geometry and is independent of the applied concentration gradient (Mohajeri *et al.*, 2010; Smith *et al.*,2004). The last term$(\partial c_1/\partial x)$ is the porewater concentration gradient.

The membrane is assumed to be a small layer of negligible thickness. The flux across the the membrane is proportional to the product of the permeation speed with the concentration difference across the membrane :

$$\frac{\partial c_i}{\partial t} = \frac{k^m}{F}\left(\frac{\partial c_i}{\partial x}\right)_{membrane} \tag{4}$$

where k^m is the permeation speed (assume to be a constant), F the form factor ($F = V/A$, where V and A are the volume and the membrane covered exchange area of the diffusion chamber, respectively).

By combining Eq. (2) and Eq. (3), taking into account of the definition of the effective diffusivity, the following time-dependent differential equation for diffusion in the sediment is obtained :

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x}\left[D^{eff}\frac{\partial c_1}{\partial x}\right] \qquad \text{in } \Omega_1 \tag{5}$$

and in the dialyser :

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x}\left[D_0\frac{\partial c_2}{\partial x}\right] \qquad \text{in } \Omega_2 \tag{6}$$

where c_1 and c_2 are concentrations of the species in domains 1 and 2 respectively. t is the time variable.

The boundary and initial conditions are written in the form

$$c_1 = C_0 \text{ in } \Omega_1, \quad c_2 = 0 \text{ in } \Omega_2 \quad \text{for } t = 0 \tag{7}$$

$$\text{on } x = 0 \quad \frac{\partial c_2}{\partial x}n = 0 \quad \text{for } t \geq 0 \tag{8}$$

$$\text{on } x = l \quad \frac{\partial c_2}{\partial x}.n = -k_m\left(c_1(x=l) - c_2(x=l)\right) \quad \text{for } t \geq 0 \tag{9}$$

$$x \to \infty \quad c_1 = C_0 \quad \text{for } t \geq 0 \tag{10}$$

where the dialyser cell is in $x \in [0,\ l]$, n is the unit normal, and the porous medium is in $x \in [l,\ \infty[$. In Eq. (5), a source/sink term for the concentration of species can be added, it is neglected in this approach.

The effective diffusivity in Eq. (5) is estimated by dividing the free-water value by the tortuosity squared τ^2 (Bally *et al.*, 2004; Bally *et al.*, 2005). The tortuosity was estimated empirically from the porosity ϕ by Boudreau (Boudreau, 1996) :

$$\tau^2 \simeq 1 - 2\ln(\phi) \tag{11}$$

This relation Eq. (11) is the best least-squares fits of experimental data and is universally representative of the tortuosities in fine-grained unlithified sediments.

3.1.2. Dimensionless equations

In the process of homogenisation all the variables will be normalised with respect to the characteristic length l, concentration at infinity C_0 and diffusion in free-water D_0.

Let us introduce the following representation of the dimensional variables appearing in Eqs. (5)-(10) where the tilde ˜ denotes the dimensionless variables

$$\tilde{c}_i = \frac{c_i}{C_0} \quad i = 1, 2, \qquad \tilde{t} = \frac{D_0 t}{l^2}, \qquad \tilde{x} = \frac{x}{l} \tag{12}$$

The governing equations take the following form :

$$\frac{\partial \tilde{c}_1}{\partial \tilde{t}} = \frac{1}{\tau^2}\frac{\partial^2 \tilde{c}_1}{\partial \tilde{x}^2} \qquad \text{in } \Omega_1 \tag{13}$$

and in the dialyser :

$$\frac{\partial \tilde{c}_2}{\partial \tilde{t}} = \frac{\partial^2 \tilde{c}_2}{\partial \tilde{x}^2} \qquad \text{in } \Omega_2 \tag{14}$$

and the boundary condition :

$$\tilde{c}_1 = 1 \text{ in } \Omega_1 \quad \tilde{c}_2 = 0 \text{ in } \Omega_2 \quad \text{for } \tilde{t} = 0 \tag{15}$$

$$\text{on } \tilde{x} = 0 \quad \frac{\partial \tilde{c}_2}{\partial \tilde{x}}.n = 0 \quad \text{for } \tilde{t} \geq 0 \tag{16}$$

$$\text{on } \tilde{x} = 1 \quad \frac{\partial \tilde{c}_2}{\partial \tilde{x}}.n = -\tilde{k}_m\left(\tilde{c}_1(\tilde{x}=1) - \tilde{c}_2(\tilde{x}=1)\right) \tag{17}$$

$$\tilde{x} \to \infty \quad \tilde{c}_1 = 1 \tag{18}$$

It is worth noting that the mathematical model Eqs. (13)-(18) is one-dimensional. The accuracy of this natural approximation can be readily justified by the fact that concentration gradients in the porous medium adjacent to the peeper in horizontal direction (x-direction) are much greater than gradients along the vertical direction (y-direction). This could be understand by the fact that the sediment are deposited in horizontal layers without vertical mixing in the bottom layers. Thus, the coefficient of diffusion D^{eff} must be replaced by a tensor which should be diagonal (Boisse *et al.*, 2007; Lecoq *et al.*, 2011) with coefficient along the y-direction lower than the one in the x-direction. This assumption is validated "a posteriori" by calculating the fluxes in all directions under the assumption of equal coefficient of diffusion.

The dimensionless equations (13–18) are solved using a finite difference numerical method (Lecoq *et al.*, 2013).

3.2. Physical parameters and sensibility tests

The model sensibility has been tested under several conditions allowing to emphasize the impact of fluctuation of modeled variables (Lecoq *et al.*, 2013). Furthermore, these variables should be integrated into the numerical model in order to fit with the measured solutes fluxes within a sediment. The final objective is to evaluate the peeper optimal equilibration time for a given sediment.

In order to adjust the numerical model with the best solute diffusion computing, the physical parameter values controlling the diffusion within the porous media, e.q. the sediment, such as permeability coefficient, porosity, tortuosity are taken from the literature and then recalculate to obtain the best model calibration befitting with it actually in place within estuary environment sediments. Others parameters such as temperature or porosity, permeation speed of the membrane are chosen among experimental field data. The input parameters are summarized in Table 2.

Parameter	Values used into the model	Units
Diffusion coefficients		
$D_0\ (SO_4^{2-})\ (T = 28^o\ C)$	11.6	$10^{-6}\ cm^2.sec^{-1}$
$D_0\ (Ca^{2+})\ (T = 28^o\ C)$	7.62	$10^{-6}\ cm^2.sec^{-1}$
$D_0\ (Mg^{2+})\ (T = 28^o\ C)$	7.77	$10^{-6}\ cm^2.sec^{-1}$
Tortuosity		
τ^2	1.96 – 2.25	
Permeation speed		
k^m	0.43	$m.s^{-1}$
Dynamic viscosity of water		
$\eta\ (T = 28^o\ C)$	0.000833	$kg.s.m^{-1}$
Equilibrium concentration		
$C_0(SO_4^{2-})$	2000–2500	mg/l
$C_0(Ca^{2+})$	400–500	mg/l
$C_0(Mg^{2+})$	1200–1500	mg/l

Table 2. Physical parameters used in the model Eqs. 12–18

The diffusion coefficients of ions in water at T=25C are obtained from the results of Li and Gregory (1974). The diffusion coefficients of ions in water at the experimental temperature of Somone is estimated from the Stokes-Einstein relation.

Results of the Ca^{2+} and SO_4^{2-} profiles of concentration obtained with the diffusion model Eqs. 12–18 are given in Fig. 7. We choose specifically these two ions because the concentrations and diffusion coefficients are quite different (table 2). Nevertheless, the peeper concentration follows the same dynamic, this indicates that the convection is negligible as it was assumed previously. On both delay times (3 or 7 days), it is clear that the equilibrium is not reached for both ions; for Ca^{2+}, only fluctuations around the mean value are observed, whereas for SO_4^{2-} a slope indicates a small vertical gradient over the depth.

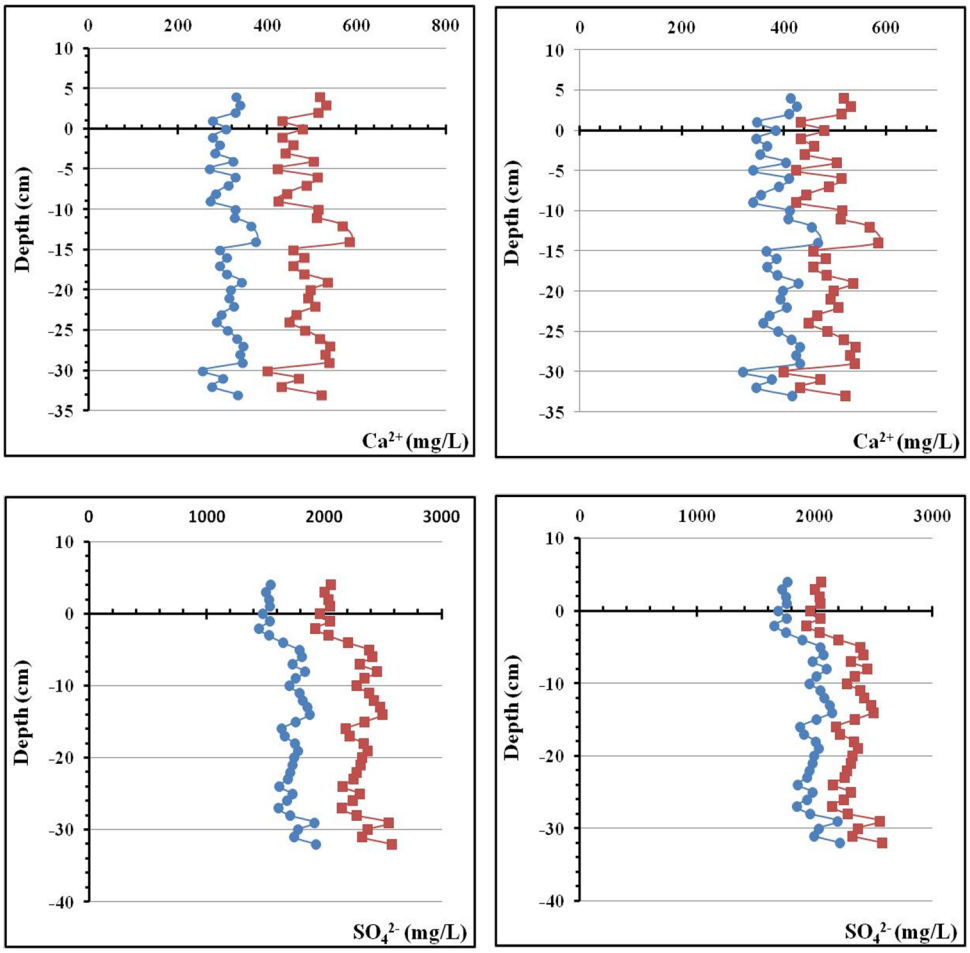

Figure 7. Modeling of peeper equilibration, for Ca^{2+}; bottom for SO_4^{2-}. Left : blue-disk curve, after 3 days; red-square curve, equilibrium is reached. Right : blue-disk curve, after 7 days; red-square curve, equilibrium is reached.

3.3. Comparison with data set

The concentrations measured in the peeper experiments are displayed with the prediction from the diffusion model in Fig. 8. The model shows a good reproduction of the evolution of profiles concentration of Ca^{2+}, Mg^{2+} and SO_4^{2-} from experimental data after 11 days.

Considering the Mg^{2+} profiles after 11 days of equilibration, the modelled concentrations exhibit slightly higher values than the *in situ* values. Nevertheless, the model results confirm the equilibration time obtained with the experimental data. Thus, we can retain a optimum equilibration time of 11 days for sampling sediment porewaters of the Somone mangrove.

However, this time is strongly influenced by the season. During the wet season, especially during the months of August and September, heavy rains cause a significant dilution of porewaters, mainly in the top 10 cm of the sediment compartment. The current diffusion

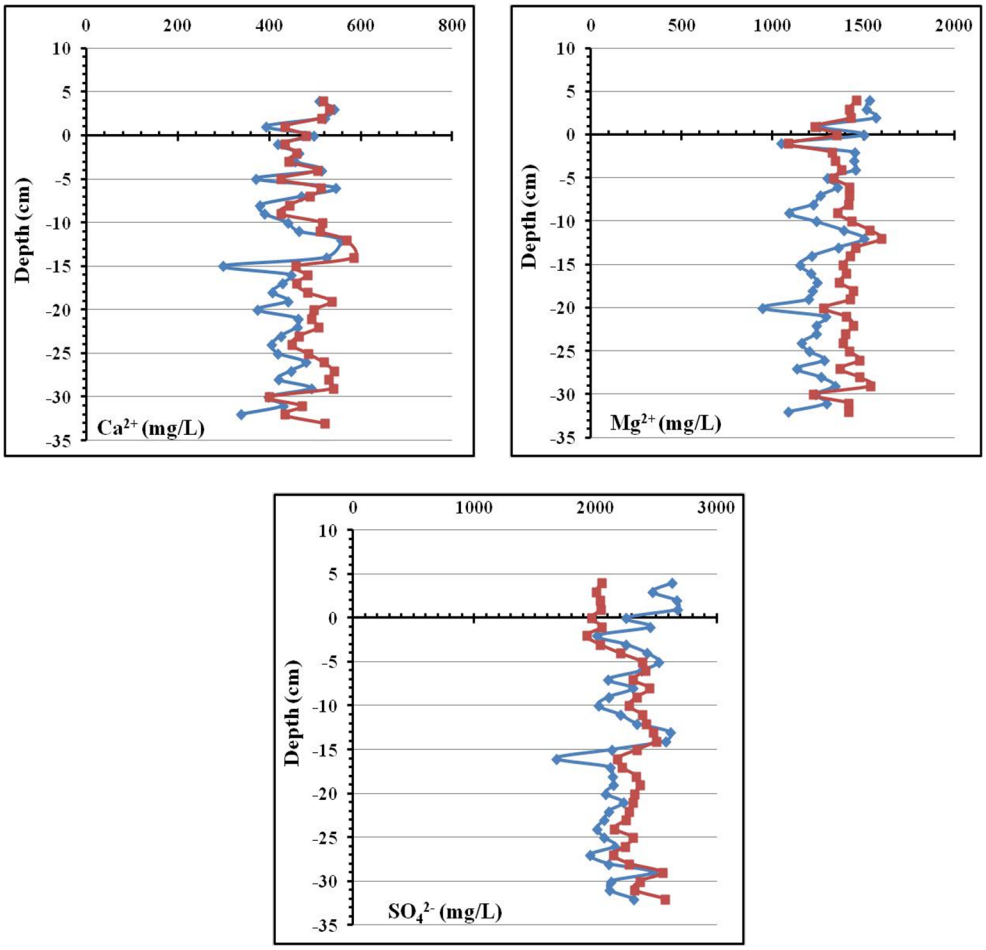

Figure 8. Vertical model profiles of Mg^{2+}, Ca^{2+} and SO_4^{2-} and experimental values in the sediment porewaters of the Somone mudflats; blue-diamond curves correspond to experimental data obtained after 11 days, red-square curves are the results of the model based on the data of equilibrium.

model developed in this chapter overcomes this limitation of the dialysis porewater sampler method.

4. Conclusions

The study of the chemical quality of the sediment porewaters of mangroves can be achieved through different techniques. The choice of technique depends on the research objectives. Each technique has limitations as in the application, the time resolution or the depth.

The peepers developed since 1976 to estimate the concentration of dissolved elements in porewater, ignore physical forcing high frequencies. This technique is widely applied today, sometimes in combination with other techniques for measuring the quality of porewater in

order to better understand porewater diffusion.

Developed for nutrients, this technique is now being applied to metals and organic compounds especially to follow the contamination of soils and sediments. The advantage of the peeper technique is to measure a mean concentration, without taking account microvariation, with a good vertical resolution over 30-40 centimetres deep. A disadvantage of this technique is the equilibration time needed to get the right concentrations in the chambers, which is problematic especially in highly reactive environments such as sediments of mangroves which can lead to excessive consumption of nutrients trapped in chambers.

This study, on Somone estuary covered by a tropical mangrove area, propose to calculate the optimized time of *in situ* measurements, using a physical diffusion model developed thanks measurements carried out in the estuary. The diffusion model needs as input a low number of estimated parameters, porosity and temperature. From these parameters, the equilibration time can be evaluated, and peepers can be used efficiently without waiting this time. The diffusion model developed in this chapter overcomes the limitation of a long equilibration time of the dialysis porewater sampler method.

The optimisation of the extent of equilibration time, reduce the time measurements of nutrients not reaching the threshold of balance. Thus in highly reactive environments, the use of peepers combining with a diffusion model is very effective and can measure with few errors the vertical concentration gradient of nutrients. This could also be applied to other dissolved elements not presented in this study and allow to calculate an accurate diffusive flux at the sediment-water interface.

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