

## Sampling pore water at a centimeter resolution in sandy permeable sediments of lakes, streams, and coastal zones

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### Abstract

Concentration gradients in the solid fraction and pore water of modern sediments allow to identify benthic biogeochemical processes and the associated fluxes. Gradients are often obtained from layers sampled below the sediment–water interface from sediment cores. Numerous examples in the literature show results from cores collected in impermeable porous sediments, but very few from permeable sediment cores. Indeed, the acquisition of vertical profiles in sandy permeable sediments with a spatiotemporal resolution equivalent to that of muddy sediments is a challenge. We present here a simple protocol that allows sampling of sandy sediments and their interstitial waters with a vertical resolution of 1 cm. This method is suitable for shallow environments, such as intertidal zones, lakes, lagoons, and stream beds. The method is based on rapid conditioning of hand-collected cores. The cores are pre-cut lengthwise. Immediately after recovery, they are laid horizontally, opened, and sliced. Interstitial water is collected by centrifugation on site shortly after cutting the core with tubes equipped with a 0.2  $\mu\text{m}$  membrane. Optimally, 30 min is sufficient between core collection and conditioning of 12 sections of a 20-cm long core. The examples shown indicate that the method is reproducible. Reduced dissolved compounds such as Fe(II), Mn(II), and  $\text{NH}_4^+$  show profiles without significant oxidation. At the time of core cutting, small volumes of pore water are seeping out of the core, but for sediments with a permeability of up to  $10^{-10} \text{ m}^2$ , this seepage does not disturb the shape of the pore-water profiles.

Profiles of dissolved and particulate compounds below the sediment–water interface (SWI) provide important information on aquatic ecosystems. They generally show gradients of reactive compounds. These gradients allow identification of benthic biogeochemical reactions and quantification of fluxes based on sediment properties such as porosity, permeability, and diffusion coefficient of the species under consideration. This knowledge provides information on early diagenesis reactions and their relationship to environmental quality, flux, and sequestration of biogenic compounds and contaminant behavior. For example, the mineralization of organic matter in sediments results in the consumption of electron acceptors, such as oxygen, nitrate, iron, and manganese oxides or sulfate, the accumulation in pore water of recycled compounds, such as dissolved inorganic nitrogen (DIN), phosphorus (DIP), and carbon (DIC), or reduced compounds such as  $\text{H}_2\text{S}$ ,  $\text{Fe}^{2+}$ , and  $\text{Mn}^{2+}$ , and finally the precipitation of authigenic phases. The contribution of benthic processes to the cycling of biogenic

elements at the ecosystem scale is variable. In all cases, they define the burial rate of biogenic compounds in sediments (Ingall and Jahnke 1994; Kennedy et al. 2010; Asmala et al. 2017). In shallow environments, benthic recycling may be largely dominant over the organic matter mineralization processes that occur in the water column (Middelburg et al. 1996; Viaroli et al. 2008; Smith et al. 2011). For these reasons, the study of benthic biogeochemistry has been widely developed for more than 40 yr, both in marine environments (Nissenbaum et al. 1972; Sholkovitz 1973; Froelich et al. 1979) and lake environments (Gächter et al. 1988).

Most studies of benthic processes have focused on the most reactive sediments, those rich in organic matter. These are usually fine sediments of low permeability. However, permeable sediments have been shown for more than 20 yr to be effective bioreactors, even though their organic matter concentration is lower (Boudreau et al. 2001; Anschutz et al. 2009; Santos et al. 2012, Huettel et al. 2014). Pore-water circulation enhances organic matter degradation though high filtration rates, advective transport of particulate and dissolved organic matter, oxygen and nutrients, oscillating redox conditions, and a bacterial community associated to sand grains (Huettel et al. 2003). These properties allow an efficient recycling of organic carbon, nitrogen, sulfur, and metals

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(Findlay 1995; Barnes et al. 2019; Mouret et al. 2020). Permeable sandy sediments represent important surfaces on continental margins, intertidal areas (Riedl et al. 1972; Luijendijk et al. 2018), and river beds where hydrodynamics are important. Methods for sampling sediments and their pore waters in this type of sediment, however, encounter a number of pitfalls.

There are several techniques, each of which can provide partial information on all the parameters needed to study benthic biogeochemistry. They can be divided into two parts: in situ methods and ex situ methods. In situ methods have the advantage of limiting the disturbances inherent in the removal of material from its environment, but they have the disadvantage of not being able to sample the solid fraction of sediments (Viollier et al. 2003). Many techniques allow direct measurement of dissolved compound concentrations using ion-selective and voltammetric micro-electrode or micro-optode probes. Compounds sensitive to these probes are measured along profiles across the SWI, with a vertical resolution that can be very fine, down to a few micrometres (Revsbech and Jørgensen 1986; Luther et al. 1998; Glud 2008). The main techniques for in situ pore-water sampling are dialysis methods (Hesslein 1976; Carignan 1984; Jannasch et al. 2004) and high spatial resolution versions: diffusive gradients in thin films (DGT) and diffusive equilibration in thin films (DET) techniques allow in situ determination of pore-water concentration profiles (Davison et al. 1991, 1994; Krom et al. 1994), or two-dimensional images of the distribution of dissolved compounds (Robertson et al. 2008, Cesbron et al. 2014). Extraction by rhizons (Seeberg-Elverfeldt et al. 2005; Shotbolt 2010) and by suction filtration samplers (Makemson 1972, Sayles et al. 1973, Charette and Allen 2006; Beck et al. 2007) are also methods often used to extract pore-water in situ, particularly in permeable sediments. Most of the in situ methods have been used in shallow (with scuba divers) or exposed sediment. For deeper waters, in situ pore-water sampling or profiling devices have been carried out using benthic landers (Reimers 1987; Fones et al. 2001).

Ex situ methods are based on the study of sediment cores taken at the SWI. There are several types of coring techniques that allow the first decimeters of sediment to be sampled with an undisturbed SWI. An exhaustive synthesis was carried out by Schulz (2006). These include box corers of various sizes, tube corers operated by various mechanisms, and multi-tube corers that allow up to eight interface core tubes to be brought to the surface from deep water. At shallow depths, the sediment tubes can be retrieved manually by divers.

In order to obtain vertical profiles of dissolved constituents in the pore water of sediment cores, the most common method is to extrude and slice the sediment cores horizontally from the interface to the bottom of the cores and extract the pore water and then analyze the dissolved compounds by standard methods. The advantages of this method are numerous. The main one is that it allows to associate each pore-water sample of a given section with the solid fraction

associated with that section. Thus, on the same core, for example, vertical DIP profiles can be plotted with the particulate phases involved in the geochemistry of phosphorus, such as organic matter, iron oxides, and authigenic phosphate phases (Schuffert et al. 1994; Ruttenberg 2014). An additional advantage is that this technique often provides sufficient water recovery per section, allowing the analysis of a maximum number of reactive compounds. Finally, this method produces profiles as long as the length of the sediment cores collected. This is an advantage, because while the fluxes at the SWI are determined by the gradients at this interface, the reactions responsible for the gradients can find their explanation in some depth, such as anaerobic respiration processes or the precipitation of authigenic phases. The extraction of pore water also has disadvantages. One is the impossibility of measuring reliable dissolved oxygen concentrations in this material (but oxygen profiles can be obtained using microelectrodes on undisturbed cores) and the other is that the vertical resolution is limited by the possibility of properly cutting slices of sediment. Generally, the vertical resolution below the SWI is at best 5 mm. These drawbacks are minor in view of all the knowledge that has been gained from the study of pore water extracted from sediment cores over 40 yr.

The two main methods for the extraction of pore water from slices of sediment cores are squeezing (Reeburgh 1967; De Lange 1992) and centrifugation. Both methods yield quite identical results (Schulz 2006). These methods require precautions to obtain reliable results. Problems may be related to temperature changes, oxygen contamination, or too long time intervals between core sampling and water extraction. These pitfalls can be avoided, for example, by working in an environment thermostated to the in situ temperature, by cutting the cores under a glove box filled with inert gas (Edenborn et al. 1986), or simply by working very quickly, when possible, which limits temperature changes and contact with oxygen. In fact, the choice of techniques for pore-water sampling should be dictated by the objectives of the study (Azcue and Rosa 1996).

The choice of methods is also constrained by the nature of the sediments themselves. In terms of methods, there is a big difference between muddy and permeable sediments. Muddy or silty sediments with a porosity greater than 50% and low permeability are much easier to recover as sediment cores than sandy sediments. One reason is that muddy sediment is generally cohesive and impermeable: the sediment itself acts as a seal, preventing pore water from flowing by gravity through the sediment core. The principle of cutting cores into horizontal slices is often based on the installation of an appropriate piston at the bottom of the core. This piston is then pushed upward to bring the sediment to the top of the core tube, allowing the protruding slice to be cut. The piston, which can be a simple plastic or polystyrene disc, can be pushed upward because the muddy sediment does not block the slide of the piston. Furthermore, the piston does not need to have a diameter precisely adjusted to the diameter of the core, since the

cohesive sediment acts as a seal and lubricant at the same time. When the sediment is sufficiently cohesive, it is possible to cut lengthways sections of horizontally placed cores and subsample them to obtain vertical profiles of pore-water and solid fraction compounds. This is not suitable for sampling fluid muddy sediments near the SWI, but has been often used in oceanography on long cores retrieved via gravity corers or IODP drilling (De Lange et al. 1992; Manheim and Sayles 1974). Once the slices of sediment are recovered, they can be squeezed or centrifuged to extract the pore water. In the course of centrifugation, the sediment will be compacted in such a manner that a supernatant of pore water can be decanted.

All this is impossible with sandy sediments. The main reason for this is that these sediments cannot be compacted by pressure exertion or centrifugation because the sand grains are already arranged in a compact way (Schulz 2006). The second reason is that these sediments possess a high degree of permeability so that as soon as a core is extracted from its medium, the pore water can percolate downward. The base of the core must therefore be quickly sealed. But it is very difficult to seal a sand core with a piston because of the grains of sand. Also a piston gets easily stuck in a sand core, which prevents the sediment from being pushed upward to cut horizontal sections. For this reason, it is very difficult to recover pore water with high vertical resolution from permeable interface sediment cores. A method for the extraction of pore water from coarse, sandy material by centrifugation is described by Saager et al. (1990) and has been used in several studies, especially on sediments from the Wadden Sea (Gehlen et al. 1995; Slomp et al. 1997; Portielje and Lijklema 1999; Rusch et al. 2000; Dellwig et al. 2007; Al-Raei et al. 2009). However, this technique does not solve the problem of how to bring a sample of sand and its pore water into a centrifugal unperturbed. To our knowledge, there are very few papers that describe vertical profiles of particulate and dissolved compounds in pore water at the SWI from cores of sandy sediments with a resolution comparable to what can be found for muddy sediments. These include studies using the method of Saager et al. (1990) and other works on coastal or freshwater environments (Marinelli et al. 1998; Jahnke et al. 2005; Deborde et al. 2008; Canton et al. 2010; Buquet et al. 2017), whereas there are thousands of such studies on muddy sediments. The method of Marinelli et al. (1998) and Jahnke et al. (2005), named in the following text “M&J method,” is based on core barrels that were fitted with rubber septae at 1-cm intervals so that pore-water samples can be obtained with minimal core disturbance by insertion of a needle attached to a small syringe. The sealing of the core, which is necessary to prevent the pore water from percolating downward, is ensured by a piston that has two O-rings. This method only allows the recovery of 3 mL of water. It only works if the sediment is very sandy (if there is a large silty fraction, the needle of the syringe is quickly clogged), and it does not allow the recovery of the solid fraction in parallel, because it is impossible in the presence of sand to push the piston

upward to bring the sediment to the top of the core tube in order to cut layers of 1 cm.

In general, pore-water extraction from permeable sediments is rather based on in situ methods such as dialysis, rhizon extraction, or suction filtration (Seeberg-Elverfeldt et al. 2005; Charette and Allen 2006; Beck et al. 2007; Gao et al. 2010; Sokoll et al. 2016) or piezometers (Rodellas et al. 2018), because these methods are facilitated by the permeability of the sediment. These methods have less potential for artifacts compared to pore-water extraction from sediment cores. Dialysis-based methods require an equilibrium time of several hours or days depending on cell size, which is not compatible with dynamic porous media, such as intertidal areas or stream beds. The vertical resolution of piezometer-based techniques is at best 5 cm. Rhizons allow a centimetric vertical resolution to be obtained, but for this, the speed of pore-water extraction must be slow (0.1–0.5 mL min<sup>-1</sup>; Seeberg-Elverfeldt et al. 2005). For the abovementioned techniques, the simultaneous recovery of the solid fraction is more complicated, because it requires the collection of a core in parallel to the in situ pore-water extraction site anyway (Stelzer et al. 2011).

In order to be able to study the vertical evolution of dissolved and particulate compounds in relation to benthic biogeochemical processes in low-porosity permeable sediments with centimeter vertical resolution, we have designed a very simple protocol that can be applied in sites where cores can be extracted manually. In this paper, we describe in detail the material used and the field manipulations required to sample and condition the pore water and sediment at a centimeter resolution over 20 cm in less than 1 h. Examples of profiles obtained in sandy sediments from a lake, an intertidal beach, a stream bed, and a coastal lagoon are presented. We present a validation of the method for pore-water extraction by comparing it with an alternative method inspired by the M&J method.

## ***Use materials and procedures***

### **Core collection**

Since pore water percolates easily along permeable sediment cores once they are removed from their environment, the way to keep the pore water at their level during core slicing is to lay it horizontally. To do this, the cores used are PVC tubes 10 cm in diameter, 3 mm thick, and 30 to 50 cm long that have been previously cut into two half-cylinders. The two halves are taped together with adhesive tape. A band of tape is applied at the joints inside the tube along the core and another one outside so that the reconstituted cylinder is leak-proof. The whole is reinforced by one turn of tape at the top and another at the base of the core. We use 50-mm-thick orange PVC tape. The base of the core is beveled to facilitate penetration into the sediment.

The core is pushed into the sediment manually. This is possible at low tide in intertidal areas or below a depth of less than 1 m in streams, lagoons, tidal channels, etc., or at greater

depths with the intervention of divers. In immersed areas, once the core is inserted into the sediment leaving 10 cm of supernatant water, a rubber bung is placed at the top. The core can be removed by suction. As soon as the core is out of the sediment, another rubber bung is inserted into the bottom firmly, while keeping the core upright in the water (the top rubber bung is removed to allow the bottom one to be pushed in). When working in an exposed environment, the core that is inserted into the sediment is retrieved by digging next to the core, allowing it to be removed from the sediment. As soon as the core is out of the sediment, it is placed on a rubber bung that is firmly inserted. The tightness of the bung at the base of the core is not always guaranteed once the core is out of the water because of the sand. For this reason, the core should be cut as quickly as possible as soon as it is retrieved, that is, as soon as it has been extracted from the sediment, which is possible on a tidal beach at low tide, or on the edge of a stream from which the core was taken, or on a sufficiently large boat when the core is brought up by divers.

When present, the supernatant water is quickly removed by siphoning off. A water sample can be recovered with a 50 mL syringe to supplement the bottom water that is collected in situ. A polystyrene stopper is placed on the surface of the sediment. This stopper is roughly adjusted to the diameter of the core so that it is not watertight. Thus, by placing it on the surface of the sediment, we prevent the air at the surface from being compressed, which could break the seal of the bottom plug. We use stopper cut with a cutter from 4-cm-thick polystyrene isolation panels. This piston is rinsed with in situ water before being placed on the surface of the sediment. Its role is only to maintain the sediment for the next operation.

### Sample conditioning

The core is laid with a joint facing upward and with the stopper applied to the sediment surface. This taped joint is cut with a cutter along the entire length and thickness of the tube so as to cut the tape that has been applied to the inside of the core. Then, the sediment is separated in half with a spatula through the cut joint. The core is then opened. The result is two half cores next to each other (Fig. 1). The core is photographed and markings are made on the central border between the two core halves. These markings guide the slicing of the core. We routinely cut 1 cm sections on the first 4 cm, then 2 cm below. For each layer, we place an aliquot in a preweighed 20-mL scintillation tube which is used to measure the water content. This sample is also used to analyze particulate compounds. Another aliquot is used for pore-water extraction. For this purpose, we use a 50-mL centrifugal tube equipped with a 0.2  $\mu\text{m}$  polyethersulfone membrane in the middle of the tube (Vivaspin<sup>®</sup> 20, Sartorius-Germany, or Macrosep<sup>®</sup> Advance Centrifugal Device, PALL Corporation). These tubes fit centrifuges that accept standard 50-mL conical end tubes. These centrifugal filters are ready-to-use commercial single-use versions that are simpler to operate than the



**Fig 1.** Photos taken by the authors showing different steps during the handling of the cores. (1) The 10 cm diameter PVC tube separated into two half tubes joined together with tape has just been inserted into the intertidal sediment of Lancieux Bay. (2) After being removed from the sediment, the core is placed horizontally in a tray. The bottom of the core is sealed with a bung, the top is held in place with a piston. The tape has been cut lengthwise and the sediment is separated in half with a spatula. (3) The preweighed vials and the centrifugation tube of vivaspin<sup>®</sup> type have been prepared in advance in order to be able to condition the core slices quickly. (4) The open core, showing the two half cores, is photographed before being sliced.

system described by Saager et al. (1990). The sample volume is 20 mL, which allows for the recovery of 5 to 10 mL of pore water. The scintillation tube and the centrifugation tube are inserted horizontally into the sediment of one half-core to the specified sample thickness. A plastic knife is used to stop the insertion of the tubes. Approximately 5 g of wet sediment is placed in the scintillation tube, while the upper part of the centrifugation tube is filled (20 mL) without headspace. We avoid taking samples close to the wall of the PVC tube. The rest of the sediment slice of the two halves is removed with the knife and we start again with the next layer. If the tubes are prepared in advance, the cutting takes 1 min per section, which limits the flow of pore water in most permeable sediments. A 20 cm core separated into 12 samples is cut in less than 12 min. The bottom slice of the core near the rubber

bung is discarded because it may be contaminated with supernatant water when the bung is placed.

The scintillation vials are placed in an icebox and frozen as soon as possible. Centrifuge tubes are also placed in the icebox and then centrifuged as soon as possible. In the field, we use two benchtop centrifuges (Hettich Rotofix 32A, equipped with a rotor 1624) powered by a small generator. This allows us to centrifuge eight samples simultaneously. Pore waters are extracted by centrifugation at  $2000 \times g$  for 10 min. The recovered water is already filtered. Two aliquots are placed in the 5 mL polypropylene vials. One is frozen (on the field, we use a freezer that plugs into the vehicle's lighter) and the other is acidified with 1/100 v/v 1 N HCl, to bring the pH around 2.

### Validation measurements

In order to validate our method, we compared it to a much less invasive method inspired by the one published by Marinelli et al (1998) and Jahnke et al (2005). For this purpose, we collected on each site two 20-cm-long cores separated by a distance of 2 m. One core was conditioned according to our method. The second core consisted of a 10 cm diameter PVC tube with a row of perforation. The holes (1 cm diameter) were aligned in a vertical column and covered with plastic tape in the inner and outer face of the core. The distance between the center of each hole was 2 cm. Just after sediment sampling, pore-water samples were collected using a needle/syringe assembly. The needle was inserted into each hole through the tape, and pore water was withdrawn slowly with minimal core disturbance by pulling back gently on the syringe plunger. This method allows water to be sampled only if the sediment is coarse enough to prevent the syringe needle from clogging. Those from the Nasseys River site had an average grain size of  $440 \mu\text{m}$ , large enough for the M&J method to work well. We were able to collect 2 to 3 mL of pore water. The sediment from the Lancieux Bay had a median grain size of  $170 \mu\text{m}$ , which did not allow us to collect pore water at all depths, and when we were able to extract it, we only obtained about 1 mL. Pore-water samples were filtered immediately through syringe membrane ( $0.2 \mu\text{m}$  pore size), placed into clean vials, and conditioned in the same way as the pore-water extracted by our new method. When we had enough sample, we measured dissolved iron, ammonium, nitrate, and phosphate concentrations. This was possible for the Nasseys cores. For the Lancieux Bay core, we measured dissolved iron first, then ammonium when there was enough sample left.

### Analyses

In this section, we briefly present the analytical methods we used for the cores described as examples in the Results section. These methods are routine for the solid fraction and have been described elsewhere. For pore water, they are optimized for low sample volumes.

The water content of the sediment was determined from the difference in mass between water-saturated wet sediment

and lyophilized sediment in the preweighed vials. The porosity ( $\varphi$ ) was calculated using the formula:

$$\begin{aligned} \varphi &= \text{pore volume} / \text{total volume} \\ &= (m_w/d_w) / [(m_w/d_w) + (m_{\text{part}}/d_{\text{part}}) - (m_w(S/1000)/2.2)] \end{aligned}$$

from the mass of water ( $m_w$ ) and its density ( $d_w$ ) and the mass ( $m_{\text{part}}$ ) and density ( $d_{\text{part}}$ ) of the particles. The typical density of the sand is  $2.65 \text{ g cm}^{-3}$ , which corresponds to the density of quartz and is close to that of calcite and feldspar (Berner 1980). The formula takes into account the salt which precipitates from the salinity (S) of the pore water when the sample is dried, with 2.2 being the density of salt. Particle size was determined by laser diffraction using a Malvern particle size analyzer in combination with a liquid sample auto-sampler. Sediment permeability  $k$  was not measured directly, but  $k$  (in  $\text{m}^2$ ) was estimated using the Kozeny–Carman equation, which is one of the most widely used equations for predicting permeability for sediments with fairly uniform size distributions (Freeze and Cherry 1979):  $k = 5.6 \times 10^{-3} \varphi^3 d^2 / (1 - \varphi)^2$ , where  $d$  is the geometric mean grain size (Urumović and Urumović 2016).

Particulate sulfur and total carbon were measured on the freeze-dried sediment by infrared spectroscopy using a LECO C/S 200. Particulate organic carbon concentration was measured with the same method after removal of carbonates with 2N HCl from 50 to 100 mg of powdered sample (Etcheber et al. 1999). Solid phase samples were subjected to two different extraction techniques operated sequentially for determination of reactive particulate P, Mn, and Fe. The most reducible fraction was extracted with an ascorbate solution buffered at pH 8 (Kostka and Luther 1994; Anschutz et al. 1998, 2005). A second extraction step was carried out with 1N HCl to determine acid soluble Fe, Mn, and P (Ruttenberg 1992). About 100 mg dried sample was leached with 10 mL of ascorbate solution (50 g  $\text{NaHCO}_3$ , 50 g Na-citrate, 20 g ascorbic acid for 1 L solution) for 24 h while shaking continuously at ambient temperature. After centrifugation for 15 min at 4000 rpm, 1 mL supernatant was diluted in 9 mL 0.2N HCl solution. The remaining ascorbate solution was discarded. After rinsing with buffered  $\text{H}_2\text{O}$ , the remaining sediment was leached with 10 mL of 1N HCl solution for 24 h in the same way as in the previous step. Supernatant was diluted with water. Fe, Mn, and P were analyzed colourimetrically in leaching solutions according to Anschutz and Deborde (2016) and Charbonnier and Anschutz (2019).

The concentrations of dissolved biogeochemical and redox compounds were measured by manual methods using small sample volumes (Table 1). The idea was to be able to measure as many parameters as possible on a total sample volume that sometimes did not exceed 5 mL. Manual methods allowed control over sample volumes and avoided dead volumes of rinsing used in autosamplers. The acidified sample was used to analyze DIP, dissolved iron and manganese ( $\text{Fe}_d$  and  $\text{Mn}_d$ ), and sulfide. The frozen sample was used to measure DIN

**Table 1.** Methods used for pore-water analyses.

| Compound                        | References | Volume ( $\mu\text{L}$ ) | Range (*)             | Analysis time for 50 samples + standards |
|---------------------------------|------------|--------------------------|-----------------------|--|
| DIP                             | 1, 2       | 500                      | 0.3–30 $\mu\text{M}$  | 1 h                                      |
| $\text{Fe}_d$                   | 3, 4       | 250                      | 0.3–180 $\mu\text{M}$ | 1 h                                      |
| $\text{Mn}_d$                   | 5, 6       | 100                      | 0.3–100 $\mu\text{M}$ | 2 h + one night                          |
| $\text{SO}_4^{2-}$              | 7          | 2000                     | 25–500 $\mu\text{M}$  | 2 h                                      |
| $\text{NO}_2^-$                 | 8          | 500                      | 0.1–20 $\mu\text{M}$  | 2 h                                      |
| $\text{NO}_3^- + \text{NO}_2^-$ | 9          | 300                      | 0.2–100 $\mu\text{M}$ | 1 h + one night                          |
| DSi                             | 8          | 500                      | 0.5–100 $\mu\text{M}$ | 2 h                                      |
| $\text{NH}_4^+$                 | 10         | 500                      | 10–1000 $\mu\text{M}$ | 3 h                                      |
| DIC                             | 10         | 500                      | 0.5–20 mM             | 3 h                                      |
| Salinity                        | 11         | 100                      | 0–50                  | (§)                                      |

References: (1) Murphy and Riley (1962); (2) Anschutz and Deborde (2016); (3) Stookey (1970); (4) Viollier et al. (2000); (5) Madison et al. (2011); (6) Charbonnier and Anschutz (2019); (7) Rodier (1976); (8) Strickland and Parsons (1972); (9) Schnetger and Lehnert (2014); (10) Hall and Aller (1992); (11) refractometre: (§) done during ammonium or DIC analyses.

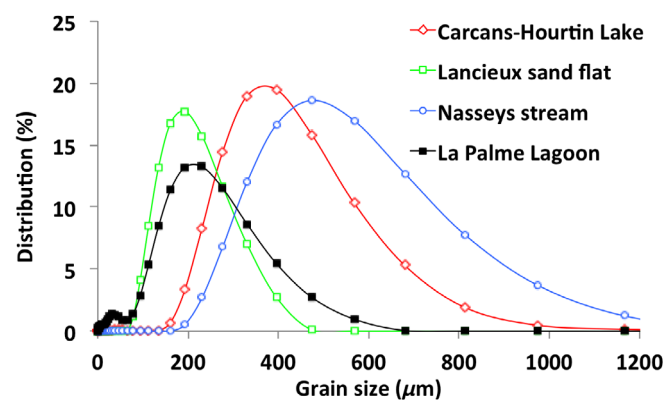
\*The value on the left represents the limit of quantification.

compounds (ammonium, nitrate + nitrite, nitrite alone), DIC, dissolved silica (DSi), and salinity. Salinity was measured for cores taken in coastal areas with a refractometer (Hanna HI96822). Ammonium and DIC were measured by flow injection analysis according to the Hall and Aller (1992) method. The other compounds were analyzed by manual spectrophotometric methods using 1.5 mL polysulfone (PS) semi-micro cuvettes with a 10 mm optical path and a Thermo Fisher Scientific Genesys 20 Spectrophotometer. This set allowed reliable absorbance measurements with a total volume (sample + reagents) of 500  $\mu\text{L}$ . The volume required for these analyses was 2.4 mL of frozen sample and 2.85 mL of acidified sample. For the latter, most of it was used for the sulfate measurement, which required 2.0 mL. This volume was required for many freshwater environments, but for marine environments, it was necessary to dilute the sample 50 times to remain within the measuring range. As a result, the sample volume used was 40  $\mu\text{L}$  and the total volume of acidified sample required for the various analyses was 890  $\mu\text{L}$  only. DSi analysis was performed last on defrosted samples. The subsample was allowed to stand at room temperature for at least 48 h for depolymerization of silica before carrying out DSi analysis.

## Assessment and discussion

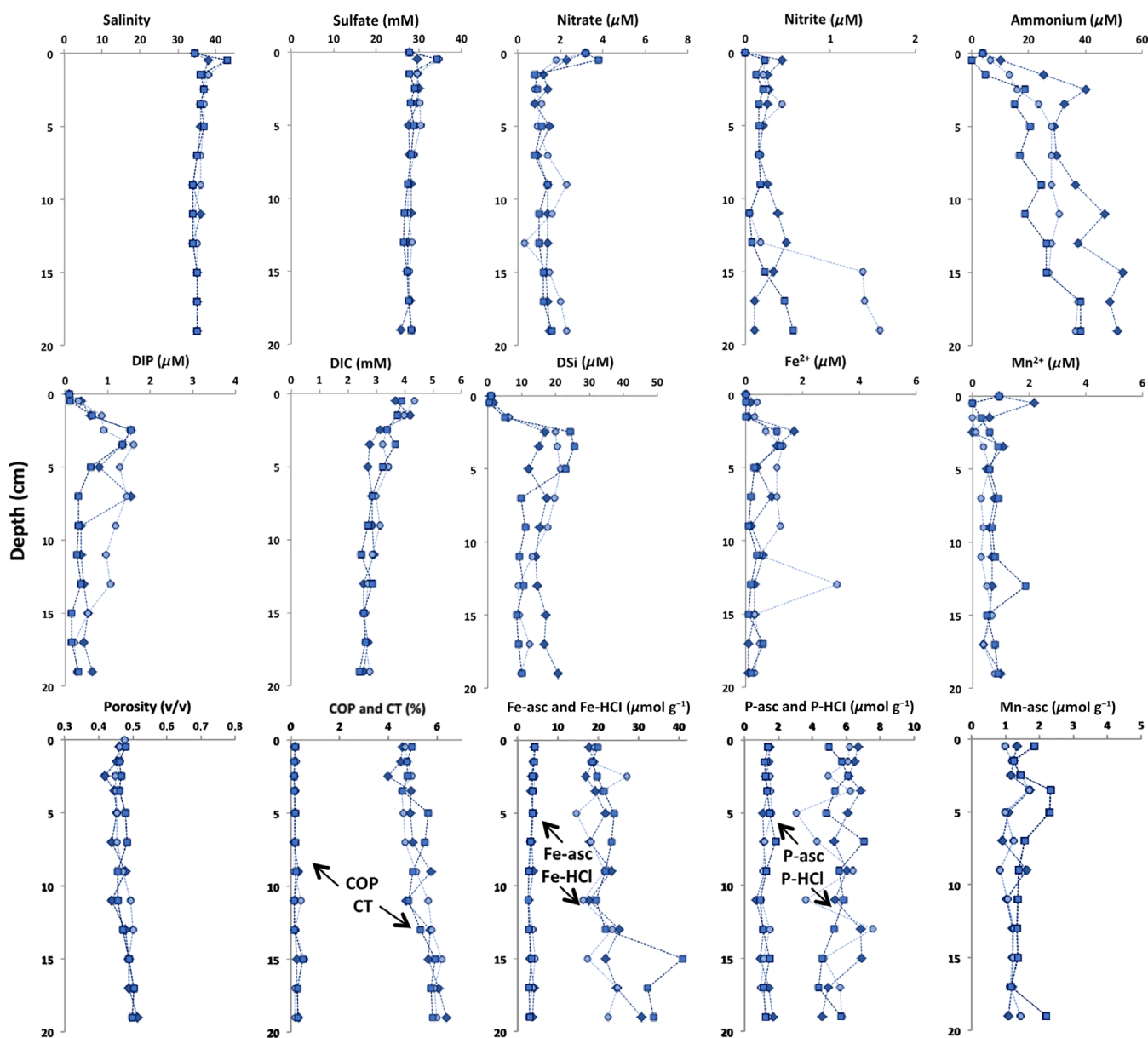
### Results from four sites

We present here examples of results acquired on permeable sediment cores taken from different types of environment in France. The first site is the U-shaped bay of Lancieux in northern Brittany, which is 3.5 km long and 1 km wide. It is a sandy tidal bay located in an area where the tides are among the highest in the world with an amplitude of up to 13 m. In April 2019, we collected three cores from the same site located 1 km from the bottom of the bay (N48.587, W2.177). The three cores were taken at low tide within 3 m of each other in a



**Fig 2.** Grain size distribution of permeable sediments of the four examples given in the text.

homogeneous area. The sediments were permeable and consisted of sands with a median grain size of 172  $\mu\text{m}$  (Fig. 2). The permeability  $K$  was  $6.5 \times 10^{-11} \text{ m}^2$ . However, the sediment surface was saturated with water at low tide due to the very weak slope of the sand flat. The cores showed a color change at about 6 cm depth from beige to gray. The results (Fig. 3) show similar profiles for the three cores. The porosity was between 40% and 50%. The profiles of the particulate compounds were relatively straight, except for total carbon which increased from an average value of 4.7% at the top to 6.1% at 18 cm depth. Organic carbon contents were around 0.2%, meaning that most of the total carbon was inorganic carbon. Since carbon represents 12% of the mass of  $\text{CaCO}_3$ , a sediment concentration of 6% inorganic C corresponds to a content of 50%  $\text{CaCO}_3$ . The pore waters had the salinity of seawater, with however an excess of salinity on the surface, probably due to evaporation. Sulfate concentrations followed those of salinity. We noted concentration gradients of redox and biogenic compounds below the SWI. The DIP concentration



**Fig 3.** Parameters measured from three replicate cores collected in a sandy sediment of the Bay of Lancieux tidal sand flat in April 2019: Vertical profiles below the sediment–water interface of pore-water salinity, sulfate, nitrate, nitrite, ammonium, dissolved inorganic phosphorus (DIP) and carbon (DIC), dissolved silica (DSi),  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , and porosity (v/v), particulate organic carbon (POC) and total carbon (CT) in weight % of dry sediment, and particulate iron, phosphorus, and manganese extracted with ascorbate and 1N HCl leaching solutions in  $\mu\text{mol g}^{-1}$  of dry sediment (Mn-HCl, which had values close to those of Mn-asc, are not shown). For dissolved compounds, the point at the interface (depth 0 cm) represents the concentration measured in a sample collected in the bay during the previous high tide.

increased in the first 3 cm from a value close to the detection limit (Table 1) up to  $1.5 \mu\text{M}$ . The values gradually decreased below. Ammonium increased below the interface to 3 cm, and then slowly increased below. Nitrate values were below  $4 \mu\text{M}$ . The highest values were in the first cm of the cores. DSi showed stable values between 10 and  $20 \mu\text{M}$  from the sample at a depth of 2 to 3 cm. Above this, concentrations tended to be similar to those in seawater from the previous high tide (shown at depth of 0 cm in profiles of Fig. 3). DIC concentrations were

high in the first 2 cm, with values around 4 mM and values around 2.5 mM deeper. Reduced dissolved compounds such as  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  had low concentrations generally below 2  $\mu\text{M}$ . What can be retained from this example is that the triplicate cores show similar profiles: the sampling and pore-water extraction method is reproducible.

The second example comes from Carcans-Hourtin Lake. This lake is the largest in metropolitan France with a surface area of  $62 \text{ km}^2$ . It is a shallow lake that lies on a quaternary

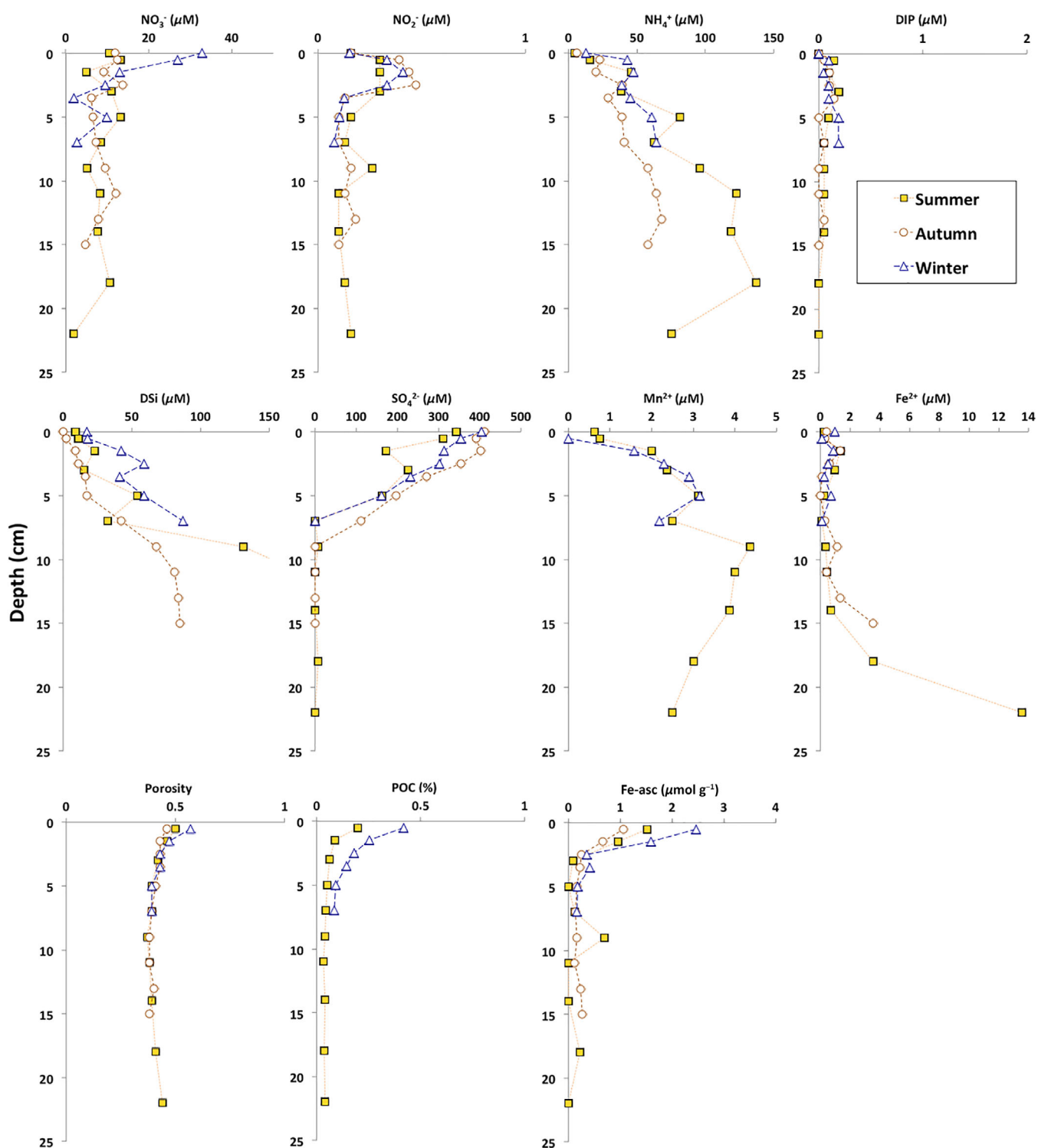
sandy substrate. Only the deepest areas have organic muddy sediments. Divers have sampled a sandy site (N45.20117, W1.11243) at a depth between 1.0 and 1.5 m depending on the season. The sand was well sorted and had a median grain size of  $413 \mu\text{m}$  (Fig. 2). Mean sediment permeability was  $13 \times 10^{-11} \text{ m}^2$ . For this site, cores were collected with the technique described above in October 2014, January 2015, and November 2015. Water temperatures were  $21^\circ\text{C}$ ,  $7^\circ\text{C}$ , and  $15^\circ\text{C}$ , respectively. These sands were greenish on the surface due to the presence of a biofilm of microphytobenthos. Organic carbon concentrations were very low at depth, with values below 0.1% (Fig. 4). At the surface, concentrations exceeded 0.2%. Surface sediments were slightly enriched in iron oxides extracted by ascorbate, with a concentration between 1 and  $2.5 \mu\text{mol g}^{-1}$  depending on the season. The P content associated with this fraction was below our detection limit. Interstitial waters showed profiles with significant gradients below the SWI, with in particular an increase in ammonium with depth, a nitrite peak below the interface and a decrease in oxidized compounds below the interface. The nitrate concentration was  $33 \mu\text{M}$  in winter in the lake water. In the interstitial water, this concentration decreased rapidly. Sulfate concentrations were between  $340 \mu\text{M}$  and  $410 \mu\text{M}$  in the lake water. They decreased linearly in the pore water and reached values below the detection limit below 8 cm.  $\text{Mn}^{2+}$  concentrations increased below the SWI, suggesting that dissolved oxygen penetration was limited to a few cm, despite the good aeration of the bottom water, the high permeability of the sediments and the agitation of the water by the waves.  $\text{Fe}^{2+}$  concentrations were rising from 15 cm depth. These observations suggest that early diagenesis processes related to the degradation of organic matter and redox reactions, in particular, aerobic oxidation, denitrification, reductive dissolution of Fe and Mn oxides, sulfate reduction, and ammonium nitrification took place in the first few cm of sediment. Despite a highly permeable environment, this example shows that if benthic processes are to be included in the mass balance of biogenic compounds in lakes, sandy cores must be studied with the same resolution as for muddy sediments. Thus, benthic fluxes can be calculated if the diffusive or advective exchange mode is known.

The third example corresponds to cores taken from the La Palme lagoon, a Mediterranean coastal lagoon of  $5 \text{ km}^2$ , and an average depth of 0.7 m. It is partially connected to the Mediterranean Sea through a small opening in the coastal sand spit, which is seasonally closed (Stieglitz et al. 2013). We manually collected cores from one site (N42.972, E3.0174) in three different seasons, in May and September 2017 and March 2018. The sediments were beige at the surface and gray below 1 cm in depth. The distribution of grain size was bimodal (Fig. 2) in the part of the lagoon studied here, with a silty fraction centered at  $35 \mu\text{m}$  and a sandy fraction centered at  $210 \mu\text{m}$ . Porosity was 60% at the surface and 50% below 5 cm depth (Fig. 5). Average calculated permeability was

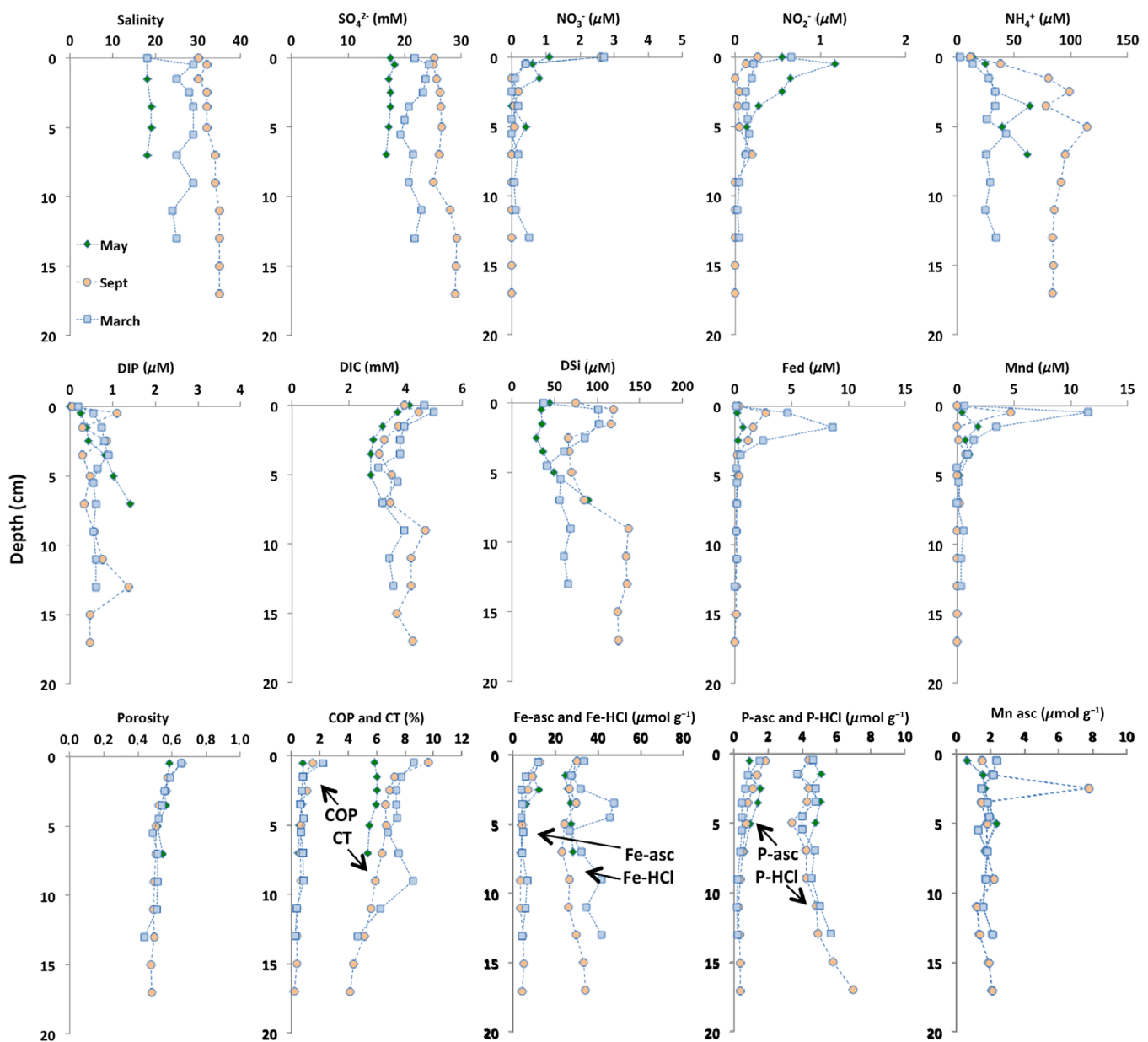
$9 \times 10^{-11} \text{ m}^2$ , which was a maximum value because of the presence of the silty fraction. The organic carbon concentration was less than 1%, except in the first cm where it could reach 2%. The first cm of sediments were enriched in iron oxides and P associated with these oxides. Interstitial waters were characterized by seasonally varying salinities, similar to the variations in salinity of the lagoon waters (Rodellas et al. 2018). The saltiest summer waters were also the richest in sulfate, ammonium, DSI and DIC. Interstitial waters were anoxic from the first cm, with peaks of dissolved  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  immediately below the interface and a decrease in nitrate concentration being observed each season. Ammonium concentrations were relatively constant at depth, between 30 and  $80 \mu\text{M}$  depending on the season. Values in the bottom water were below  $15 \mu\text{M}$ . This created a concentration gradient in the upper cm of the sediment, and thus a flux toward the water column. DIP concentrations were below  $1.4 \mu\text{M}$  in the cores studied. However, those collected in winter and spring showed a regular concentration gradient below the SWI. Recent works have shown from radioisotope fluxes that significant amounts of water from the lagoon recirculate in the sediments (Stieglitz et al. 2013; Rodellas et al. 2018; Tamborski et al. 2018). Estimated advective recirculation flows are on the order of  $0.7 \pm 0.5 \text{ m}^3 \text{ s}^{-1}$  or  $1.3 \pm 1.0 \text{ cm d}^{-1}$  (Tamborski et al. 2018). Nutrient fluxes at the SWI have been deduced from these values and the nutrient concentration measured in the pore water (Rodellas et al. 2018). For that, vertical nutrient concentration profiles were acquired in the sandy lagoon sediments from sampling using a drive-point piezometer with a vertical resolution of 5 cm near the interface (Rodellas et al. 2018). The vertical resolution with our method is more accurate. Our example shows that the maximum gradients below the SWI occur in the top centimeter of the sediment (Fig. 5). This suggests that our method could be used to refine benthic flux estimates, as a complement to studies that aim to quantify water fluxes.

The fourth example is cores taken from the bed of a stream. The Nasseys River drains a large part of the watershed of the Parentis-Biscarrosse Lake in southwestern France. The river represents the outcropping water table of the permeable surface aquifer consisting of Quaternary eolian sands. The median particle size of the quartz sands is  $370 \mu\text{m}$  (Fig. 2). A factory that manufactures activated carbon located near the mouth of the river generates a point source of N and P. Two cores were taken from the riverbed, one downstream of the factory outlet (N44.3415, W1.081) and the other upstream (N44.3347, W1.0458). The flow at the upstream point was  $600 \text{ L s}^{-1}$  on the day of sampling, which corresponded to low flows for this river, with currents of  $0.3 \text{ m s}^{-1}$ . The sandy sediments were permeable ( $10 \times 10^{-11} \text{ m}^2$ ). Porosity was between 30% and 37%. Organic carbon contents were less than 0.2% (Fig. 6). The properties measured on the solid fraction were the same for both cores, except that the first centimeters of the sediment collected downstream of the plant were rust





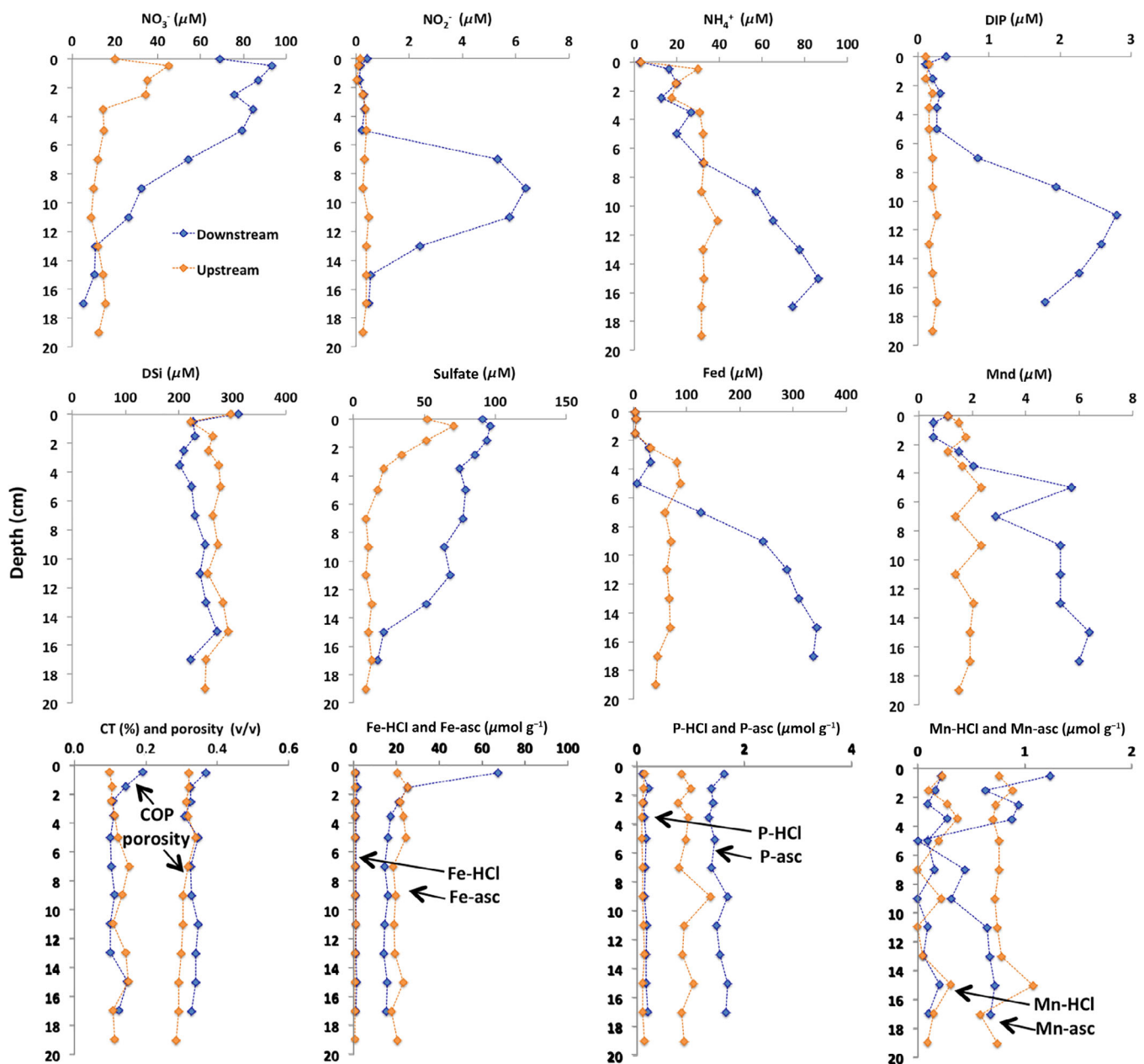
**Fig 4.** Parameters measured from cores collected in a sandy sediment of the Carcans-Hourtin Lake at three seasons in 2014 and 2015: Vertical profiles below the sediment–water interface of pore-water nitrate, nitrite, ammonium, dissolved inorganic phosphorus (DIP), dissolved silica (DSi), sulfate,  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  in  $\mu\text{M}$ , and porosity (v/v), particulate organic carbon (POC) in weight % of dry sediment, and particulate iron extracted with an ascorbate leaching solution (Fe-asc) in  $\mu\text{mol g}^{-1}$  of dry sediment. For dissolved compounds, the point at the interface (depth 0 cm) represents the concentration measured in bottom waters.



**Fig 5.** Parameters measured from cores collected in a sandy sediment of the La Palme Lagoon at three seasons in 2017 and 2018: Vertical profiles below the sediment–water interface of pore-water salinity, sulfate, nitrate, nitrite, ammonium, dissolved inorganic phosphorus (DIP) and carbon (DIC), dissolved silica (DSi), iron ( $\text{Fe}_d$ ) and manganese ( $\text{Mn}_d$ ), and porosity ( $v/v$ ), particulate organic carbon (POC) and total carbon (CT) in weight % of dry sediment, and particulate iron, phosphorus, and manganese extracted with ascorbate and 1N HCl leaching solutions in  $\mu\text{mol g}^{-1}$  of dry sediment (Mn-HCl, which had values close to those of Mn-asc, are not shown). For dissolved compounds, the point at the interface (depth 0 cm) represents the concentration measured in bottom waters.

colored and were enriched in iron oxides extracted by ascorbate and slightly richer in organic C. The average P content extracted by ascorbate was  $1.5 \mu\text{mol g}^{-1}$  downstream of the plant and  $0.9 \mu\text{mol g}^{-1}$  upstream. The pore water showed significant gradients, despite the permeability of the sediments. The core taken upstream from the source of contamination showed gradients in the first few cm and vertical straight profiles from 5 cm depth. Nitrate and sulfate decreased below the

interface, while dissolved iron and ammonium increased, suggesting that anaerobic processes of organic matter mineralization were occurring a few cm below the interface, but that at depth oxidation of organic matter stopped, due to lack of labile OM. The core taken downstream of the source of contamination showed less straight profiles than the core taken upstream. DIP, iron, and ammonium levels increased from 6 cm depth. Dissolved iron concentrations reached more than



**Fig 6.** Parameters measured from two sandy cores collected in the river bed of the Nasseys stream in November 2016. Core have been collected upstream and downstream a point source of N and P: Vertical profiles below the sediment–water interface of pore-water nitrate, nitrite, ammonium, dissolved inorganic phosphorus (DIP), dissolved silica (DSi), sulfate, iron ( $\text{Fe}_d$ ) and manganese ( $\text{Mn}_d$ ), and porosity (v/v), particulate total carbon (CT) in weight % of dry sediment, and particulate iron, phosphorus, and manganese extracted with ascorbate and 1N HCl leaching solutions in  $\mu\text{mol g}^{-1}$  of dry sediment. For dissolved compounds, the point at the interface (depth 0 cm) represents the concentration measured in stream water.

200  $\mu\text{M}$  below 10 cm depth. The profile showed a steadily increasing pattern. A nitrite peak between 7 and 13 cm depth corresponded to the decrease in nitrate below 7 cm and the increase in ammonium from this depth, suggesting that denitrification and ammonium nitrification processes occurred in this interval. Sulfate concentrations decreased regularly between the surface and 15 cm depth. This example shows that riverbed sediment is indicative of processes where river

oxic waters are in contact with anoxic waters a few cm below the interface. The observed gradients are dependent on the biogeochemical processes of mineralization of the organic matter in these sediments and the result of advective mixing in the hyporheic zone of the surface water infiltrating the permeable sands and groundwater of the anoxic groundwater table (Hester et al. 2017). The hyporheic zone is typically defined as the portion of the alluvial aquifer in which surface

water and groundwater mix (Gooseff 2010). Hyporheic exchange has long been recognized as a primary control of nutrient, carbon, and contaminant cycling in rivers and streams. The example shown here indicates that a snapshot of the concentration gradients can be obtained with centimeter vertical resolution at the top of the hyporheic zone, which can complement other methods for studying the processes specific to this interface (Cardenas 2015).

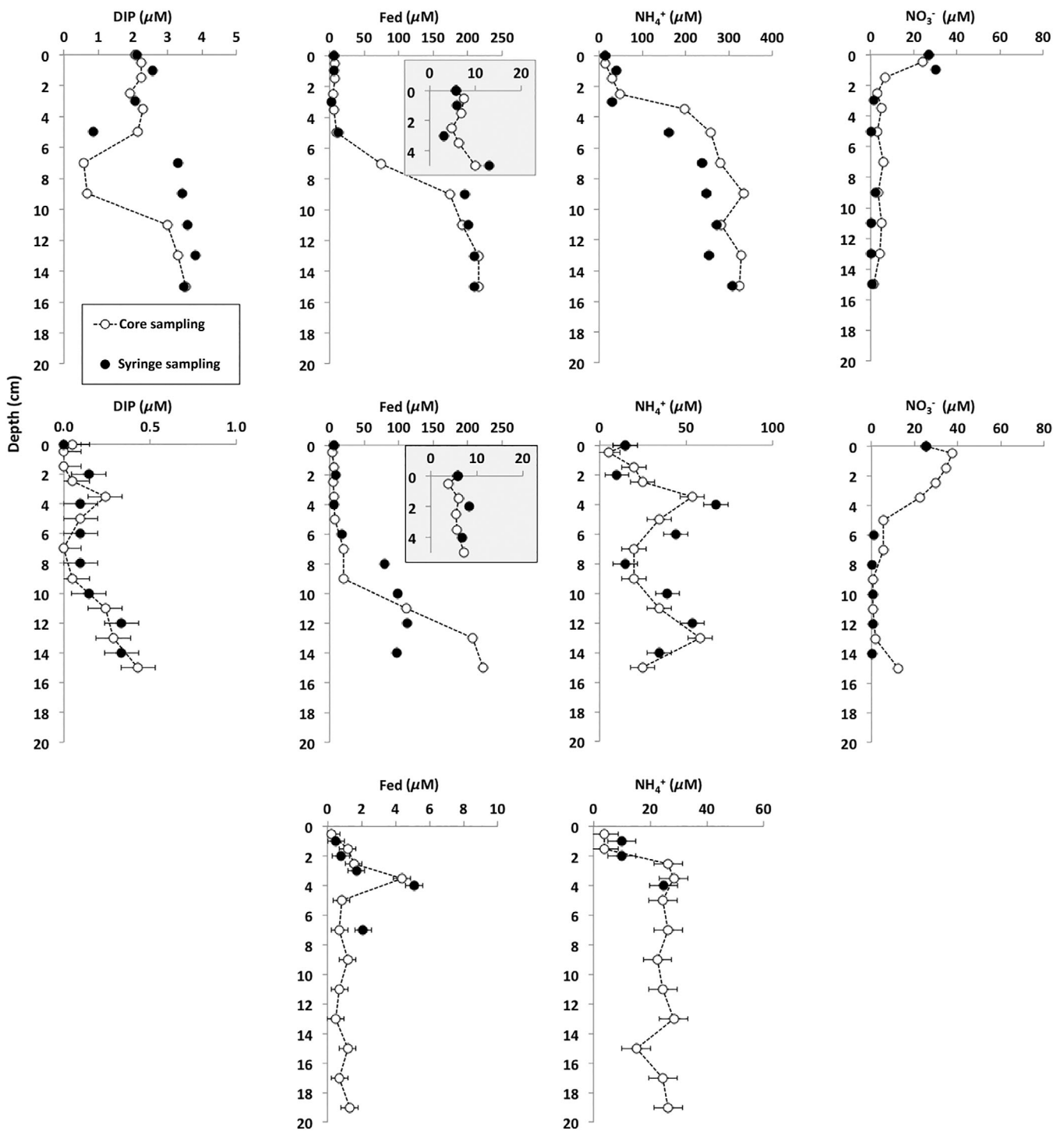
The sediments tested for validation using our method and the M&J method were sampled in September 2020 in the Lancieux tidal sand flat and in the Nasseys River. Results showed similar profiles, with few differences discussed below, which could be attributed to spatial patchiness (Fig. 7). The profiles of the compounds most sensitive to oxidation, such as dissolved iron and ammonium, showed identical shapes suggesting that the profiles obtained from the samples by our method were not affected by the oxidation of these compounds. The comparison of the profiles is limited to only a few points for the sediments of the Bay of Lancieux, because the method of extraction of pore water with the syringe method did not allow us to obtain more water than what we have exploited here. We noted a difference in the cores taken from the upstream portion of the Nasseys River, with higher dissolved iron concentrations at the bottom of the core manipulated using our method than in the core where the pore water was collected with a syringe. For the other compounds measured, the profiles overlapped.

### Reproducibility of results

The examples we have chosen to show indicate that the method of core collection and pore-water extraction gives reproducible and consistent results. The example of the three cores taken from the tidal flat of Lancieux Bay (Fig. 3) shows that the values replicate correctly. The differences between the three cores can be attributed to the patchiness that necessarily exists in intertidal areas (Mouret et al. 2016), particularly in sandy areas where there is slight surface roughness due to tidal ripples (Huettel et al. 1996). The pore waters that were extracted by our method and the M&J method in Lancieux Bay and the Nasseys River show consistent profiles. The observed differences can also be attributed to a spatial patchiness. Indeed, we observe similar concentrations. Only the depths at which gradients appear differ between the two methods (Fig. 7). The shape of the seasonal profiles acquired in Carcans-Hourtin Lake (Fig. 4) or in La Palme Lagoon (Fig. 5) show great consistency, with profiles of particulate species that do not change much, and little variation in the pore-water profiles that can be explained by changes in temperature or changes in concentration in the supernatant water column. Thus, for example, in the case of Carcans-Hourtin Lake, the decrease in sulfate concentrations due to sulfate reduction is seen each season, and peaks in nitrite due to ammonium nitrification or denitrification are observed.

### Oxidation of reduced compounds

The objective of the method implemented for permeable sediments is to be able to work very quickly in order to avoid the displacement of interstitial water. Fifteen minutes are required between core sampling and the end of the slicing process. The need for speed is opposed to a number of precautions, and in particular, the cores were not cut under an inert atmosphere. This can lead to oxidation of reduced compounds (Bufflap and Allen 1995). Cutting the core in a glove box would have significantly lengthened the core handling time and the pore water would have percolated through the sediment. Therefore, we did not use a glove box. Despite this, the reduced compound profiles do not show any anomalies. In particular, we note very regular dissolved iron profiles in the Nasseys cores (Fig. 6), suggesting that partial oxidation of this compound during pore-water extraction was not sufficient to affect the profiles, at least on the scale of the several hundred micromolars measured here. Otherwise, much more irregular profiles would have been expected. The seasonal cores from La Palme all show subsurface dissolved Fe and Mn peaks of a few micromolars that reflect reductive reduction processes of Fe and Mn oxides in the first few centimeters, with different intensities in each season. The regular shape of the peaks and their detection at each season suggests that the data are not disturbed by the method. In the Lancieux tidal flats, dissolved Fe and Mn values are more heterogeneous. But here, the concentration levels are of the order of micromolar. The hypothesis of an effect of oxidation of these compounds during pore-water extraction cannot be ruled out, but by comparing with the La Palme profiles, it can be assumed that the impact of oxidation can only affect Fe and Mn concentrations at the micromolar level. Secondly, it is not impossible to think that the variations in the concentration of dissolved Fe and Mn at Lancieux are due to patchiness. The profiles of ammonium, another reduced compound, are regular in all the cores. This suggests that this element is not oxidized during sampling and conditioning. However, ammonium would be expected to remain stable once the pore waters are filtered, as ammonium oxidation is not a fast process. Finally, comparison with the M&J method with which the pore water is immediately conditioned, without any centrifugation or transport phase, shows similar profiles. In particular for dissolved iron, the two profiles made from two neighboring cores downstream of the Nasseys River (Fig. 7 top) or in the Bay of Lancieux (Fig. 7 bottom) are similar. For the site upstream of the Nasseys River, there is a small difference: in both cases, the dissolved iron concentration increases from 6 cm depth, but the concentrations measured at the bottom of cores differ. They are 100  $\mu\text{M}$  for one profile and 200  $\mu\text{M}$  for the other. But the highest concentration is obtained with our method. Our method therefore does not show a profile degraded by an oxidation of dissolved Fe compared to the M&J method. The difference would thus be once again due to the spatial heterogeneity between the two cores studied.



**Fig 7.** Comparison between pore waters collected according to our new method (white dots), and a method adapted from Marinelli et al. (1998) and Jahnke et al. (2005) (black dots). Cores were collected downstream (top) and upstream (middle) a point source of N and P in the river bed of the Nasseys stream (same location as in Fig. 6), and in the Lancieux tidal sand flat (bottom). The upper 5 cm of  $Fe_d$  are shown on a separate scale for the Nasseys stream.

Among the reduced dissolved compounds analyzed ( $Fe^{2+}$ ,  $Mn^{2+}$ ,  $NH_4^+$ ),  $Fe^{2+}$  has the most rapid oxidation kinetics (Stumm and Morgan 1996). Dissolved Fe removal by

$Fe(II)$  oxidation exhibits a first order kinetics, which can be expressed by  $Fe^{2+} = Fe^{2+}_0 \exp(-k_1 t)$  (Stumm and Lee 1961; Davison and Seed 1983; Millero et al. 1987), where the kinetic

constant depends on pH and dissolved oxygen concentration:  $k_1 = k \text{ pO}_2 (\text{OH}^-)^2$  (Baken et al. 2015): oxidation is enhanced when  $\text{O}_2$  concentration and pH increase. The oxidation kinetics depend essentially on pH, since the term  $(\text{OH}^-)^2$  indicates that the kinetics are multiplied by 100 when the pH increases by one unit. The upper part of the centrifuge tubes is completely filled without headspace, which limits oxygen contamination. However, during centrifugation, water passes through the filter in the middle of the tube and accumulates in the lower part of the tube, which is initially filled with air. Oxidation of the reduced compounds may occur during this process. As soon as centrifugation is complete, the water is acidified, which immediately stops the oxidation of metals such as dissolved iron. The half-life of dissolved iron ( $t_{1/2} = \ln 2/k_1$ ) is several hours when the pH is below 7 in water at 5°C (Millero et al. 1987), which explains why the river and lake waters showed no signs of oxidation (the pH of the waters measured occasionally was slightly acidic). In the case of marine waters, the pH is slightly alkaline and the oxidation kinetics of  $\text{Fe}^{2+}$  is expected to be rapid. Theoretically, at pH = 8.0, a possible value in marine pore water, the half-life of  $\text{Fe}^{2+}$  in an  $\text{O}_2$ -saturated medium is a few minutes (Millero et al. 1987). For seawater at pH = 7.8, the value of  $k_1$  is  $0.004 \text{ min}^{-1}$  at 5°C, while it is  $0.2 \text{ min}^{-1}$  at 25°C. In the first case, the half-life of Fe(II) is close to 3 h, in the second case it is 3.5 min. Keeping cold therefore limits the oxidation kinetics of Fe(II). In the field, as soon as the samples are placed in the centrifuge tube, they are placed in a cool box filled with ice pack. Cold is maintained until centrifugation, which is carried out rapidly. In the examples we have described, we have aliquoted the interstitial waters into an acidified and an acid-free fraction. However, if we are only concerned with the dissolved compounds measured in the acidified sample, it is possible to place the acid in the lower part of the centrifuge tube before centrifugation. Similarly, if there is a specific interest in the measurement of dissolved sulfides, Zn acetate may be placed in the lower compartment in advance. In summary, filling the centrifuge tubes, which limits contact with oxygen in the sample mass, placing the tubes cold and conditioning the samples quickly limits the risk of oxidation of the reduced compounds. For marine waters, it is essential to centrifuge the samples as quickly as possible. In acidic pH environments, the risk of oxidation remains low and centrifugation of collected samples can wait a few hours when there is no other choice.

#### Interstitial water flow

As long as the sediment core is held vertically and sealed with a rubber bung at the bottom, water does not percolate through the sediment. As soon as the bung is removed, water can percolate very quickly through the permeable sediment. This is why we have chosen to cut the cores in a horizontal position. Our observations on sediments with permeability between 7 and  $13 \times 10^{-11} \text{ m}^2$  (corresponding roughly to hydraulic conductivities between 7 and  $13 \times 10^{-4} \text{ m s}^{-1}$ ) show

that before cutting the first slice of sediment, some pore water may seep out of the sediment. We then noted that the water no longer flows during the time it takes to cut the different slices of sediment. As a result, the first sample in the 0 to 1 cm interval may lose some water, the others may not. When the core is laid horizontally and separated into two parts, the hydraulic pressure no longer applies to the height of the core, but only to the half-width. This height is a maximum of 5 cm with the tubes we have used. As the bottom of the horizontal half-core is made of the PVC tube, the water can only flow toward the ends of the core. However, not all the water participates in the flow. A distinction is made between free water, which can move by gravity or under the effect of a pressure gradient, and bound water, retained by capillarity and hygroscopic forces. The size of the latter fraction depends on the shape, relative arrangement, and size distribution of the particles. The retention of free water depends on the hydraulic pressure and water saturation of the pore medium. When a sediment core taken from an aquatic environment is opened, the sediment is saturated with water. When the hydraulic conductivity is sufficiently high, which is the case for permeable sediments, water will inevitably seep out when the core is opened. But very quickly, the porous medium becomes unsaturated with water and the suction effect becomes important, which decreases hydraulic conductivity and quickly limits the flow of water (Van Genuchten 1980; Thiéry 2015). In summary, laying the core and dividing it in half lengthways limits hydraulic pressure. Only a limited fraction of the pore water seeps out. By the time core cutting starts, the first sample loses some water, then the next slices are cut quickly. The vertical gradients are respected, because the water does not flow through the core.

#### Comparison with other methods

We have described in the introduction a number of methods for collecting pore water below the SWI in permeable media. The major advantage of the method we propose here is that pore water and the solid fraction are collected in parallel from the same core. Water extraction by rhizon or suction methods allows the removal of large volumes of pore water. They have also been adapted to take water from sedimentary columns of several dm or several m. This is an advantage over our method. However, suction techniques have a vertical resolution well above 1 cm. The examples we have shown, where we see large gradients in the upper centimeters of sediment, indicate that if we are interested in particular in benthic biogeochemical processes close to the SWI it is important to have good vertical resolution. Our method allows this. The rhizons make it possible to obtain a vertical centimetric resolution, but for this, the speed of extraction of water from the pores must be slow ( $0.1\text{--}0.5 \text{ mL min}^{-1}$ ), which is not very good for permeable media where water can percolate, and the volume taken cannot exceed 3 mL for a 10 cm diameter core (Seeberg-Elverfeldt et al. 2005). Dialyzer-based methods also provide

centimeter resolution. However, these methods require a long equilibration time (Webster et al. 1998), which can be adapted to stable environments for several weeks, such as lake bottoms, but which is totally incompatible with non-stationary environments on a short time scale, such as intertidal environments. DGT or DET-based methods can sample pore water with sufficiently short re-equilibration times to study intertidal environments (Thibault de Chanvalon et al. 2017). In addition, these techniques offer very fine vertical resolutions. However, these in situ samplers represent physical obstacles to water flow and can modify sediment structure and concentration gradients in interstitial waters, as well as sediment micro-reliefs (Huettel et al. 1998) in river beds or coastal environments subject to currents. The M&J method allows to sample interstitial water with a good vertical resolution, but we have seen that as soon as the sediment is finer than medium sands, it does not work anymore. When we were able to extract pore water, this method and ours gave similar profiles for the measured parameters. Thus, the sampling method described in this paper is a good compromise for sampling pore water and the solid fraction in various shallow permeable sedimentary environments. The examples we have shown indicate that despite the high permeability of the sediments, pore-water profiles can exhibit significant gradients below the SWI. Although these gradients do not allow direct quantification of fluxes at the SWI when these fluxes are dominated by advective movements (Jahnke et al. 2005), the characterization of vertical profiles in pore water remains relevant information on benthic processes and on the residence times of pore water. In some cases, diffusive transport may be dominant in permeable sediments, for example, in the absence of hydrodynamics at the time of sampling, or when the surface is sealed at the interface by a biofilm or a fine particles layer. In these situations, our method become useful to calculate benthic diffusive fluxes.

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None declared.

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