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Quantification of diagenetic transformation of continental margin sediments at the Holocene time scale

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34 depositional diagenetic processes. Diagenesis of Holocene deposits also contributes to a low,
35 but significant fraction of N and P flux to the Bay of Biscay sea water.

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38 keywords: Early diagenesis; authigenesis; benthic flux; sediment recording; gravity core; Bay
39 of Biscay

40

41 **1. Introduction**

42

43 Marine sediments are made of partially degraded organic and mineral particles settling
44 from the water column. Due to permanent supply of settling particles, they are archives of the
45 evolution of sedimentation conditions. Reconstruction of ocean history from marine
46 sediments requires to use a wide range of physical, chemical or biological methods and
47 proxies (Wefer et al., 1999; Calvert and Pedersen, 2007). A proxy is a quantifiable parameter
48 recorded in the sediment, which allows us to describe a variable that cannot be directly
49 measured, such as past sea surface temperature, salinity or biological productivity.

50 During the last decades, meter-long piston cores represented the most appropriate
51 material to reconstruct Quaternary paleo-oceanography. Cores were investigated mainly for
52 their micropaleontological content and geochemical proxies distribution. Sedimentary
53 archives recorded in cores are submitted to diagenetic transformations , such as redox
54 reactions due to organic matter degradation, that can lead to misinterpretation of proxies (e.g.,
55 Donnadieu et al. 2002; Burdige, 2006; Sundby et al. 2015). The amount of knowledge on
56 early diagenetic processes is the result of several decades of works, including pioneer studies
57 of Froelich et al. (1979) on the vertical sequence of redox reactions, Berner (1980) on the
58 transport-reaction coupling, and Aller (1980) on the influence of macrofauna on
59 biogeochemical reactions and fluxes. Early diagenetic processes in marine sediments are
60 driven by the oxidation of naturally occurring organic compounds (La Rowe and Van
61 Cappellen, 2011) by microorganisms using a sequential series of oxidants in decreasing order
62 of thermodynamic energy yield (Froelich et al., 1979; De Lange, 1986; Burdige 2006).
63 Oxygen is the most favourable oxidant, and then nitrate, Mn-oxides and hydroxides, Fe-
64 oxides and hydroxides, and sulphate are used below the oxic-anoxic boundary. In recent
65 decades, many works have been published on early diagenetic processes of sediments buried
66 several metres below the seafloor (e.g. Schulz et al., 1994; Berelson et al., 2005; Chong et al.,

67 2018; Treude et al., 2014; März et al., 2008; Niewohner et al. 1998) – not to speak of the
68 numerous results on diagenesis in the deep biosphere studied in ODP and IODP drilled cores
69 (e.g., Arndt et al. 2006, d’Hondt et al. 2004).

70 Diagenesis processes cause chemical gradients and subsequent fluxes of dissolved
71 chemical compounds that may combine and exchange with the particulate phase. In this way,
72 properties of the geochemical content buried in the sediment can be modified. Are particularly
73 concerned proxies such as organic carbon (Reichart et al., 2002), nitrogen (Ganeshram et al.,
74 1995; Martinez et al., 2000), phosphorus (Ruttenberg and Berner, 1993), transition metals and
75 trace elements (Chaillou et al., 2002; Calvert and Petersen, 2007), and magnetic signal
76 (Passier et al., 1998; Garming et al., 2005). Diagenesis processes also affect biological
77 proxies. Fossilized microorganisms like foraminifera have been intensively used in paleo-
78 oceanography reconstructions, via their specific characteristics or isotopic chemistry of their
79 tests (Emiliani, 1955; Berger, 1969; Schiebel et al., 2001). Knowing calcium carbonate
80 chemistry in marine sediments is essential to calibrate these calcareous micropaleontological
81 proxies and to understand eventual changes in the geochemical properties of their shell during
82 burial (Dittert et al., 1999).

83 Early diagenesis processes in the Bay of Biscay slope have been investigated from
84 interface cores (~20 to 50 cm-long) during the last twenty years. Studies focused on suboxic
85 diagenesis (Hyacinthe et al., 2001), benthic foraminifera micro-environments (Fontanier et al.,
86 2002), trace metal diagenesis (Chaillou et al., 2002), effects of turbiditic layers (Anschutz et
87 al., 2002; Chaillou et al., 2008), benthic manganese geochemistry (Mouret et al., 2009), and
88 oxygen and organic carbon fluxes in upper sediment (Mouret et al., 2010). Completing these
89 results on the upper sedimentary layer, piston cores over 1 to 3 m in length have been
90 collected and analysed in order to characterize anoxic diagenetic processes in Holocene
91 sediments. Beyond the regional relevance of our results, the aim of the present study was to
92 determine how redox reactions linked to organic matter mineralization could change sediment
93 chemistry, and how a recorded signal could be modified in the almost steady state situation of
94 the Holocene. In this purpose, we measured a large range of particulate and pore water
95 compounds involved in early diagenesis reactions in order to determine geochemical
96 transformations from mass balance calculations based on flux estimates. This data set also
97 allowed us to assess fluxes of nutrient to the sediment surface due to deep diagenesis
98 processes.

99

100 **2. Material and methods**

101

102 **2.1. Study area**

103

104 The Bay of Biscay is located on the eastern side of the Northern Atlantic Ocean, bathed
105 by oceanic waters from the North Atlantic Drift. Several rivers in France and Spain feed the
106 sedimentary basin. The Gironde estuary and the Loire River are presently the main sources of
107 fresh water and fine sediments to the margin (Borja et al., 2019). The four stations sampled
108 (D, B, A and WH, Fig. 1) have been chosen according to a bathymetric transect from 150 to
109 2000 m water depth on the continental slope of the Landes Plateau. Stations at 150 m (D) and
110 550 m (B) water depth are under the influence of North Atlantic Central Waters (about 10-
111 12°C), whereas station A at 1000 m water depth is under the influence of Mediterranean
112 Ocean Waters (about 10°C) and station WH at 2000 m water depth is under the influence of
113 North Atlantic Deep Waters (Anschutz and Chaillou, 2009). Sediment consists of mud
114 composed of siliciclastic clay and silt, and 15 to 35 dw% (dry weight percent) of carbonates
115 (Hyacinthe et al., 2001). Sediment accumulation rates (SAR) were inferred from $^{210}\text{Pb}_{\text{xs}}$ (half-
116 life=22.3 years) activity profiles, sediment porosity, and a model based on steady-state
117 manganese diagenesis (Chaillou et al., 2002; Mouret et al., 2009). SAR decreases offshore,
118 from 50 – 80 $\text{mg cm}^{-2} \text{yr}^{-1}$ at station B, about 35 $\text{mg cm}^{-2} \text{yr}^{-1}$ at station A to about 10 mg cm^{-2}
119 yr^{-1} at station WH. At the shallowest station D, ^{210}Pb profiles indicate a maximal rate around
120 1630 $\text{mg cm}^{-2} \text{yr}^{-1}$, but this value should not be considered according to high bioturbation
121 thickness observed in the upper part of the core (Schmidt et al., 2009). Additional data
122 presented in this paper allowed us to better constraint SAR in the Bay of Biscay. Following
123 Mouret et al. (2010), the mean depth of dissolved oxygen penetration was 6 mm at station D,
124 2 cm at station B, 3.2 cm at station A, and 6 cm at station WH.

125

126 **2.2. Sampling and sample processing**

127

128 Depending on the four stations, the upper sediment was sampled 4 to 16 times between
129 1997 and 2009, with an interface multi-corer. Samplings were achieved during OXYBENT,
130 FORAMPROX and PECH cruises on board the RV “Côtes de la Manche”. The multi-corer
131 allows sampling the upper few decimetres of sediments, the overlying bottom waters, and the
132 undisturbed sediment-water interface, in a 10 cm diameter Plexiglas tube. At a given station,
133 very similar profiles of redox reactive compounds were measured in all short cores collected

134 during 10 years (Mouret et al., 2016). Only light differences were noticed at the sediment
135 surface, which were attributed to seasonality, bioturbation, or patchiness.

136

137 One to 3.5 meter long Kullenberg cores were collected in duplicate at the four stations
138 during the PROSECAN IV cruise organized in May 2007 onboard the RV “Thallia” and the
139 CADIAC1 and 2 (June and August 2009) cruises on board the RV “Côtes de la Manche”. For
140 each station, one core was sealed for later sedimentary analyses, and micropaleontological
141 studies (Mojtahid et al., 2013; Garcia et al., 2013). The second core was immediately sub-
142 sampled on board for biogeochemical analyses and ^{14}C dating. Two cm thick horizontal
143 sections were cut with a sampling step between 5 and 20 centimetres. For each level, a $\sim 5\text{ cm}^3$
144 sub-sample was immediately sealed in a pre-weighted vial, and frozen for further
145 determination of porosity and analyses of the solid fraction. Another sub-sample was
146 centrifuged on board under inert N_2 -atmosphere at 4000 rpm for 15 minutes in order to collect
147 pore waters. Supernatant was filtered ($0.2\ \mu\text{m}$ cellulose acetate syringe filter). An aliquot was
148 frozen for inorganic nitrogen compound analyses, a second aliquot was acidified with
149 ultrapure HCl for dissolved phosphate, Mn, and Fe analyses. During the CADIAC cruises,
150 sampling was realized for pore water methane analyses: 5 cm^3 sediment was sealed in a pre-
151 weighted glass vial with 1 mL 1M NaOH.

152

153 **2.3. Analyses**

154

155 Grain size was measured every 5 cm using a laser diffractometer Malvern Mastersize. A
156 1 cm thick slab was sampled along the core length and X-radiographed using the Scopix
157 system (Migeon et al., 1999), which consists of an X-ray imaging system combined with
158 image analysis software.

159 Three or four sediment sub-samples were collected along the cores and sieved through
160 $150\text{-}\mu\text{m}$ mesh screen for foraminifera picking. Radiocarbon dating was performed by UMS-
161 ARTEMIS (Pelletron 3MV) AMS facilities (CNRS-CEA Saclay, France) on hand-picked
162 *Globigerina bulloides*, *Neogloboquadrina pachyderma* or on the bulk planktic foraminifera
163 assemblage, according to the microfauna of each sample. The ^{14}C age (^{14}C yr BP) was
164 converted to calendar age (cal yr BP) using the Fairbanks program version 0107 (Fairbanks et
165 al., 2005) taking into account a reservoir age of 400 years.

166 Maximum sediment mass accumulation rate of station D core was estimated from
167 profiles of $^{210}\text{Pb}_{\text{xs}}$ with depth. Activities of ^{210}Pb and of its radioactive parent, ^{226}Ra , were

168 determined in about 4–6 g of freeze-dried material sealed in a counting vial, by high-
169 resolution and low-background gamma spectrometry for 4–24 h (Jouanneau et al. 1998;
170 Schmidt et al. 2007). The γ detectors were calibrated with IAEA RGU-1 reference materials.
171 Supported ^{210}Pb was obtained from ^{214}Bi and ^{214}Pb peaks. By subtracting the activity of ^{226}Ra
172 from the ^{210}Pb total specific activity, we obtained the unsupported ^{210}Pb component, and we
173 used it to determine accumulation rates. The gamma spectra of samples also gave the ^{137}Cs
174 activity, which was useful for core D to determine the modern sediment layer deposited for
175 the last 60 years.

176 Porosity was calculated from particle density and water content determined by
177 comparison of the weights of wet and dried (lyophilised) sediment. Particle density was
178 estimated at 2.65 (Berner, 1980), which is the mean density of alumino-silicate and calcium
179 carbonate minerals. The dried solid fraction was homogenized and water content was used to
180 correct analyses for the presence of sea salt that precipitated during lyophilisation. Particulate
181 sulphur and total carbon were measured on the freeze-dried sediment by infrared spectroscopy
182 using a LECO C/S 200. Particulate organic carbon (POC) concentration was measured with
183 the same method after removal of carbonates with 2N HCl from 50 mg of powdered sample
184 (Etcheber et al., 1999). Particulate inorganic carbon is the difference between total and
185 organic carbon. In core WH, because of the presence of 2N HCl refractory carbonates,
186 carbonate content was measured by a calcimetric method. Particulate organic carbon was then
187 deduced by the difference with the total carbon. Solid-phase samples were subjected to two
188 different extraction techniques for determination of reactive solid-phase Mn and Fe. The most
189 reducible fraction (Fe-asc and Mn-asc) was extracted with an ascorbate solution buffered at
190 pH 8 (Anschutz et al., 2005). A second extraction on a separate aliquot was carried out with
191 1N HCl to determine acid soluble Mn (Mn-HCl) and Fe (Fe-HCl). For ascorbate and 1N HCl
192 procedures, about 100 mg dried sample was leached with 10 mL of solution during 24-h while
193 shaking continuously at ambient temperature. The supernatant was diluted ten times with
194 0.2N HCl for ascorbate extraction, and with water for HCl extraction. Mn-HCl represents the
195 whole fraction of Mn-oxides and Mn associated with carbonates. Mn-asc represents the major
196 part of reducible Mn (III, IV) oxides and oxyhydroxides. Iron extracted with HCl comes from
197 the fraction extracted by ascorbate, FeS, some iron phyllosilicates and carbonates. Phosphorus
198 was also measured in leaching solutions. P extracted with ascorbate (P-asc) derives from P
199 associated with Fe-oxides extracted with ascorbate (Anschutz et al., 1998). P extracted with
200 HCl represents inorganic particulate P, i.e. P associated with iron oxides, carbonates and
201 lithogenic and authigenic phosphate minerals (Ruttenberg, 1992).

202 Pore water compounds were analysed using techniques adapted for small volumes of
203 samples. Nitrate was measured by flow injection analysis (FIA) according to Anderson
204 (1979). Ammonium and dissolved inorganic carbon (DIC) were analysed with the FIA method
205 described by Hall and Aller (1992). Sulphate was measured with a nephelometric method
206 using BaCl₂, and Fe²⁺ with the colorimetric method using ferrozine (Stookey, 1970).
207 Phosphate in pore water and in leaching solutions was measured by a colorimetric method
208 according to Anschutz and Deborde (2016). Manganese was measured by flame atomic
209 absorption spectrometry (FAAS, Perkin Elmer AA 300) using an external aqueous standard
210 for calibration. Calcium was also determined by FAAS using Lanthanum chloride as matrix
211 modifier (Haswell, 1991). Methane was measured using a gas chromatograph (Hewlett
212 Packard HP 5890A). The reproducibility of analyses was better than 5%.

213

214

3. Results

215

216

3.1. Sedimentary and biostratigraphic observations

217

218 The sediment-water interface was well preserved in interface cores collected with the
219 multi-corer, whereas the upper centimetres of sediment from the Kullenberg cores were lost.
220 To estimate this sediment loss in cores used for biogeochemical analyses, we compared the
221 profiles of reactive compounds, such as ammonium, dissolved Mn and Mn-asc, or the
222 porosity profiles measured in the Kullenberg cores with profiles from the interface cores. In
223 this way, we were able to correct the vertical scale, with a precision of ±1 cm. All depths cited
224 here are corrected depths. Core taken in duplicate at each site for sedimentological and
225 micropaleontological analyses

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X-ray images showed a clay/silty-clay facies for all studied sites. At station D, muds
were dark brown down to 133 cm and became black below. The mean grain size of particles
was between 10 and 15 µm (Fig. 2). At the deeper station B, sediment also showed moderate
grain size variations. The mean grain size of particles was 10 µm in the upper 20 cm. It was
between 10 and 15 µm down to 3 m depth, and reached at 18 µm at the bottom. At station A,
sediment was silty clay except between 60 and 80 cm depth, where a silty sand facies
occurred. The mean grain size of the sediment particles was around 5-6 µm in the clay facies
and reached 35 µm in the silty sand layer. At the 2000 m depth station WH, the sediment was
quite homogeneous along the core, with a mean grain size around 6 µm. Histograms of grain

235 size frequency have been realized for all stations. They indicate an unimodal distribution with
236 a major mode between 6 and 10 μm depending on the stations. Two discreet secondary modes
237 at 30-40 μm and 200 μm can be observed and are attributed to silt and fossilized foraminifera
238 fraction, respectively.

239 Radiocarbon measurements along the cores gave ages between 173 ± 92 and 16437 ± 128
240 cal years. Core WH and A recorded the entire Holocene period within less than 1 m. The
241 beginning of the Holocene corresponded to the silty-sand facies between 60 and 80 cm depth
242 in core A. At station B, the 320 cm long core contained Holocene sediment, since an age of
243 8990 ± 32 cal years measured at 280 cm depth. Sediments of the shallow core D gave
244 inconsistent ^{14}C ages. The presence of detectable $^{210}\text{Pb}_{\text{xs}}$ levels at 96 cm depth, and the
245 occurrence of the man-generated ^{137}Cs isotope at 56 cm depth showed that the 2 m long core
246 D contained modern sediments. The $^{210}\text{Pb}_{\text{xs}}$ activity decreased with a slope that corresponds
247 to a sedimentation rate of 0.76 cm yr^{-1} . The mass accumulation rate, deduced from the
248 sedimentation rate and the cumulated particle mass deduced from the porosity gradient, was
249 $0.63 \text{ g cm}^{-2} \text{ yr}^{-1}$, suggesting a deposition of the bottom sediment of the core D 270 years
250 before sampling.

251 At stations D, B, WH and the first 80 cm of station A core, planktic foraminifera
252 assemblage was composed by a typical fauna of subtropical/temperate areas (*Globigerina*
253 *bulloides*, *Orbulina sp.*, *Globorotalia truncatulinoides* (sinistral)). The high abundance of
254 *Turborotalia humilis*, which is only observed during the Holocene period in the Bay of
255 Biscay, indicated that the time period sampled was less than 10 000 years, in agreement with
256 ^{14}C dating. In the core A, planktic foraminifera assemblage below 113 cm depth was
257 dominated by the subpolar/polar species *Neogloboquadrina pachyderma*.

258

259 **3.2. Reactive solid fraction**

260

261 Particulate organic carbon content was between 2.2 dw% and 1 dw% in surficial
262 sediments (Fig. 3). The highest values were measured in the shallowest station cores (D and
263 B). POC content decreased with core depth, and at 1 m depth it reached 1.4 dw% at station D,
264 0.8 dw% at station B, 0.4 dw% at station A, and 0.5 dw% at station WH (Fig. 3). For all sites,
265 particulate sulphur values increased with core depth. In the first centimetre, particulate
266 sulphur concentrations remained close to $10 \mu\text{mol g}^{-1}$ and reached at 120 cm depth $70 \mu\text{mol g}^{-1}$
267 at station B, $32 \mu\text{mol g}^{-1}$ at station A, and $55 \mu\text{mol g}^{-1}$ at station WH. At station D,
268 particulate sulphur values reached $100 \mu\text{mol g}^{-1}$ within 20 cm and reached a maximum of 189

269 $\mu\text{mol g}^{-1}$ at 176 cm depth, in the dark zone of the sediment. For a given station, HCl and
270 ascorbate extractions showed vertical profiles with similar shapes, but HCl extraction were
271 more concentrated in Fe, Mn and P than ascorbate extractions. Profiles showed a subsurface
272 maximum, and quite constant and lower values below. At station D, extracted Fe and P values
273 increased at around 130 cm depth and remained steady below (Fig. 4).

274 At stations A and B, Mn-asc and P-asc values remained low in the anoxic zone, whereas
275 Mn-HCl and P-HCl, increased slightly with core depth (Fig. 4). Mean particulate inorganic
276 carbon concentrations increased with the water depth, ranging from 2 dw% at station D to 4
277 dw% at station WH. The corresponding CaCO_3 content varied between 16 and 33 dw%,
278 respectively (Fig. 3). At station A, CaCO_3 concentration of Holocene sediment was twice the
279 concentrations measured downcore below 80 cm (pre-Holocene sediments).

280

281 **3.3. Pore water composition**

282

283 The pore space, that defined the porosity (Φ), showed a logarithmic decrease downcore
284 (Fig. 2). Between the surface and 1 m depth, porosity decreased from 0.86 to 0.67 at station
285 D, from 0.85 to 0.57 at station B, from 0.84 to 0.61 at station A and from 0.86 to 0.62 at
286 station WH. A minimal value of 0.55 at 68 cm depth was observed in core A, corresponding to
287 the silty sand zone.

288 Dissolved redox compounds showed the well established distribution (Froelich et al.,
289 1979), in which oxic compounds, such as nitrate and sulphate, decreased with depth (Fig. 5),
290 and reduced compounds, such as dissolved iron, manganese, and ammonia were below or
291 close to the detection limit in the oxic layer, and their concentrations increased below.
292 Recycled compounds, as dissolved inorganic phosphorus (DIP) and DIC increased with depth
293 (Fig. 5). More precisely, bottom water concentrations of nitrate increased with water depth
294 from 4 μM at station D to 33 μM at station WH. Nitrate concentration decreased steeply
295 below the sediment-water interface, but concentrations always remained above the detection
296 limit in the anoxic part of the sediment column, between 1 and 5 μM . Sulphate remained close
297 to sea water concentration at the top of the cores. Downcore profiles indicated a slight
298 decrease at the deeper stations (A and WH), with respective values of 29 and 25 mM at 110
299 cm depth. At station B, sulphate decline was stronger, with a concentration of 10 mM at 210
300 cm depth. At station D, sulphate were completely consumed, with values below detection
301 limit below 160 cm depth. Recycled compound concentrations, such as ammonia, DIC and
302 DIP, increased more sharply at the shallower stations (D and B) than at deeper stations (A and

303 WH). These concentrations remained close to sea water concentrations at the surface
304 sediment, and then they increased with depth. So, ammonia concentrations at 1 m depth
305 reached 2000 μM in core D, 1500 μM in core B, 164 μM in core A and 390 μM in core WH.
306 Respective concentrations of DIC at the same depth were 15 mM, 9 mM, 3.0 mM and 2.2 mM
307 whereas DIP concentrations reached 20 μM , 19.7 μM , 2.5 μM and 6.5 μM , respectively.
308 Reduced dissolved compounds, as iron, manganese and sulphides, were observable all along
309 the Kullenberg cores. Dissolved iron concentrations showed maximal values at the top of the
310 cores just below the oxic layer (between 30 to 120 μM), then decreased and became lower
311 than 10 μM at depth, except at station D, where concentrations increased again down to 200
312 cm depth and reach 30.6 μM at 196 cm depth. Dissolved manganese concentrations increased
313 in the first decimetres of sediments, with a maximum at 2 cm depth at station D, 8.5 cm depth
314 at station B, 18 cm depth at station A and 25 cm depth at station WH. Deeper in the sediment,
315 dissolved manganese concentration decreased to values less than 10 μM below 1 m depth.
316 Dissolved calcium concentrations were close to the sea water value of 10.5 mM at the top of
317 sediment cores and decreased steadily with depth. The higher gradient was observed at station
318 D, where values reached 1.75 mM at the bottom of the 2 m-long core. Pore water methane
319 concentration had constant and low values for all samples, except below 150 cm depth at
320 station D (584 μM at 178 cm depth and 366 μM at the bottom of the core, Fig. 5).

321 To summarize, station D is characterized by quite large organic matter concentrations
322 (>2%), a weak oxygen penetration depth and a complete consumption of sulphate at 150 cm
323 depth. Downcore, methane concentrations increase strongly. Dissolved compounds directly
324 produced by organic matter mineralization increase with depth, whereas dissolved manganese
325 and calcium concentrations decrease. Station B shows moderate organic carbon
326 concentrations (POC = 1.9% at the surface sediment), dissolved oxygen penetrates deeper in
327 the sediment (2 cm) and a significant sulphate decreasing gradient occurs, even if sulphate is
328 not completely consumed downcore. The same trends are observed for recycled dissolved
329 compounds and dissolved manganese and calcium. Station A is characterized by quite weak
330 POC contents (POC = 1% at the core top), a dissolved oxygen penetration depth of 3.2 cm
331 and the presence of the Holocene-Pleistocene transition between 60 and 80 cm depth. This
332 transition layer is observable on some profiles, with an increase in ascorbate and HCl
333 extracted phosphorus, manganese and iron (Fig. 4), and a decrease in POC and carbonate
334 concentrations (Fig. 3). However, ammonia, DIP and DIC concentrations increase regularly
335 with depth and sulphate and dissolved calcium values decrease slightly. Dissolved manganese
336 profile shows a strong decrease with depth. Station WH is characterized by a POC content

337 less than 1.5% at the core top, and a dissolved oxygen penetration depth of 6 cm. Recycled
338 dissolved compounds, sulphate, dissolved calcium and manganese profiles show similar
339 trends than at station A.

340

341 **4. Discussion**

342

343 **4.1. Sediment accumulation rate**

344

345 Sedimentation appears to remain steady throughout the Holocene period, since no
346 interruption of sediment structure could be observed, and the profiles of reactive particulate
347 compounds, as POC or Fe and Mn content from HCl leaching show a regular shape. The 3 m-
348 long core B and the 1.25 m-long core WH have recorded the Holocene period, with ^{14}C ages
349 at the bottom of the cores of 8982 ± 32 and 12113 ± 67 cal years BP respectively (Fig. 2). At
350 station A, Holocene deposits constitute the top 70 cm of the core (11230 ± 20 cal years BP at
351 73 cm depth), and the end of the last glacial period is recorded downcore with a radiocarbon
352 age of 16437 ± 128 cal years BP determined at 161 cm depth. The transition between these two
353 periods is marked by a silty sand layer, probably due to strong fluvial discharges linked to
354 European ice sheet melting (Eynaud et al., 2007). Dissolved element concentrations do not
355 show any change around this transition, because past gradients are smoothed by molecular
356 diffusion (DeLange, 1983). At station D, ^{210}Pb data of the top meter of sediment suggest
357 that the entire sedimentary column at site D has been deposited during the last 270 years.

358 In the Holocene sequence in the Bay of Biscay, carbonates consist mainly of marine
359 microorganism remains (Garcia et al., 2013). Carbonate content is quite constant at a given
360 site. However, an obvious offshore-onshore gradient occurs with values around 35% at the
361 deepest stations (A and WH), more than 20% at station B and 12% at station D (Fig. 3). The
362 shallowest site D is under continental influence with sedimentation dominated by silicoclastic
363 supplies that decline offshore supplanted by bio-production of carbonates.

364 Porosity data allow us to integrate the inventory of particles over the whole length of the
365 long cores. Considering a mean particle density of 2.65 (Berner, 1980) and an horizontal
366 section of 1 cm^2 , this inventory is about 182 g from the top to the bottom of core D, 360 g in
367 core B, 65.5 g in the Holocene sequence of core A and 103 g in core WH. Using the ^{14}C
368 dating recorded at the bottom of the cores, we obtain that the mean mass accumulation rate
369 (MAR) is $40\text{ mg cm}^{-2}\text{ yr}^{-1}$ at station B, $5.8\text{ mg cm}^{-2}\text{ yr}^{-1}$ in the Holocene period of station A

370 and 8.5 mg cm⁻² yr⁻¹ at station WH. At station D, ²¹⁰Pb_{xs} data give a MAR of 630 mg cm⁻² yr⁻¹. Values of MAR inferred from our core analysis, integrating long-term sedimentation, can be
371 compared with results obtained from surface sediment data, as ²¹⁰Pb_{xs} dating, ages deduced
372 from the Mn diagenesis model (Mouret et al., 2009), or mass fluxes calculated from sediment
373 traps deployed in the water column (Schmidt et al., 2009). At station B, fluxes deduced from
374 ¹⁴C dating are about two times lower than results from surface methods (50 to 80 mg cm⁻² yr⁻¹);
375 at station A, MAR from ¹⁴C dating is about one order of magnitude lower compared to
376 other methods (35 mg cm⁻² yr⁻¹). At station WH, all methods give exactly the same results.
377 Such discrepancy at stations B and A suggests that dating and deduced mass fluxes based on
378 methods used in surface sediment are affected by surface processes. For instance, ²¹⁰Pb_{xs}
379 dating of station WH, A and B was most probably overestimated in previous studies because
380 of bioturbation-induced particle mixing in the upper part of the sediment column (Soetaert et
381 al., 1996). Except station D, radiocarbon ages can be considered as the most confident date to
382 calculate mean MAR in Holocene sediments because they are acquired far below the
383 bioturbation zone.
384

385

386

387 **4.2. Diagenetic sequence**

388

389 Interface core data show that oxygen concentrations decrease rapidly below the
390 sediment-water interface (Mouret et al., 2010). Nitrate strongly decreases below the layer that
391 contains oxygen. The disappearance of oxygen and nitrate goes along with a decline of the
392 Mn-oxides and Fe-oxides content and an increase in dissolved manganese and iron. Deeper
393 down the Kullenberg long cores, sulphate content decreases linearly. At station D, sulphate is
394 totally consumed and high methane concentrations appear at the bottom of the core, where
395 there is no more sulphate. This distribution follows the well-established depth sequence of
396 diagenetic reactions governed by the preferential use of the electron acceptor that yields the
397 highest amount of free energy for the bacterially mediated oxidation of organic matter
398 (Froelich et al., 1979; Postma and Jacobsen, 1996). In the following discussion we will
399 attempt to quantify processes, in which reactive compounds are involved in the Holocene
400 anoxic sediment and estimate the consequent implications for interpretation of sedimentary
401 record.

402 Previous works on dissolved oxygen profiles at the studied stations have shown that the
403 quantity of carbon mineralized by oxic processes is above POC content in the surficial

404 sediment (Mouret et al., 2010). It has been proved that POC measured in surficial sediment at
405 stations B, A and WH are remains that represented respectively only 45%, 25% and 15% of
406 settling carbon, the other part being rapidly mineralized through aerobic processes at the
407 sediment-water interface.

408 The rapid decrease in organic matter content in the upper centimetres of the sediment
409 and the profiles of redox compounds indicate that organic matter mineralization rates are
410 highest near the sediment-water interface. The occurrence of linear pore water profiles and
411 almost constant POC, Fe-asc and Mn-asc values below this reactive zone imply the existence
412 of an intermediate reaction-poor, diffusion-dominated zone. The almost linear decrease in
413 sulphate concentration suggests that a reaction zone occurs at depth. At station D, the
414 consumption of sulphate is associated with the transition between sulphate reduction and
415 methane-bearing sediments. This has been observed in many continental margin sediments.
416 Sulphate concentrations go to zero as methane diffuses upward where it is oxidized by
417 sulphate through a microbial process of anaerobic oxidation of methane (AOM) (Martens and
418 Berner, 1974; Nauhaus et al., 2002 ; Reeburgh, 2007; Knittel and Boetius, 2009). In cores B,
419 A, and WH, the transition zone between sulphate and methane was not observed, probably
420 because it occurred just below (B) or far below (A and WH) the bottom of the collected cores.
421 The depth of the transition zone may vary from less than a meter below the sediment surface
422 to several tens of metres in different settings (e.g., Iversen and Jørgensen, 1985; Borowski et
423 al., 1999; Dickens, 2001; D'Hondt et al., 2004; Hensen et al., 2003; Berelson et al., 2005;
424 Snyder et al., 2007; März et al., 2008). The depth of methane production zone is probably
425 linked to the evolution of a parameter that allows the refractory fraction of organic matter to
426 become reactive at depth. Burdige (2011) suggested that the geothermal gradient could be the
427 physical parameter that explained that refractory material becomes more reactive with depth
428 due to increasing temperature. In continental margin sediments, immense sub-surface
429 accumulations of methane can be present in the form of methane hydrate (e.g. Bohrmann and
430 Torres, 2006; Ruppel and Kessler, 2017). Methane hydrate have not been evidenced until now
431 in the southern Bay of Biscay, but emission of gas at the seafloor issuing from sub-surface
432 methane have been observed recently (Dupré et al., 2014 ; Pierre et al., 2017 ; Ruffine et al.,
433 2017).

434 Profiles of dissolved sulphate are almost linear. A slight curvature occurs at station B.
435 This can be due to a decrease in porosity with depth and a resulting decrease in diffusion
436 coefficient (Boudreau, 1996). The curvature can be directly linked to sulphate reduction
437 through anaerobic oxidation of organic matter within the layer located above the sulphate-

438 methane transition zone. Even if the curvature of the profile is not obvious in the studied
439 stations, the increasing concentration of particulate sulphur with depth suggests that sulphate
440 reduction does occur along the studied cores. Moreover, model results (Burdige et al., 2016)
441 show that linear profiles may also occur when high rates of sulphate reduction occur near the
442 sediment surface and at the sulphate-methane transition zone with low, but nonzero, rates of
443 sulphate reduction in between. At the same time, linearity in the sulphate profile may also be
444 related to downward pore-water advection by compaction and sedimentation (Burdige et al.,
445 2016). A flux of dissolved sulphate to the sediment can be calculated and then a rate of
446 organic matter mineralization through sulphate-reduction can be deduced according to the
447 stoichiometry of the reaction (two carbons for one sulphate; Burdige, 2006). The flux of
448 dissolved compounds in pore waters in steady state conditions was calculated considering the
449 vertical distribution of the dissolved compound and porosity gradient within the sediment,
450 according to Fick's first law of diffusion (Schulz and Zabel, 2006):

451

$$452 \quad J = - \Phi D_s dC/dX$$

453

454 where J is the flux, Φ is the porosity, dC/dX is the concentration gradient, and D_s is the
455 bulk sediment molecular diffusion coefficient, assumed to be equal to $D_s = D_o / [1 - \ln(\Phi^2)]$
456 (Boudreau, 1996), where D_o is the diffusion coefficient in water at *in situ* temperature (Schulz
457 and Zabel, 2006). Bioturbation and bioirrigation processes have been neglected in the flux
458 model since most diffusive processes discussed here concern sediment depth located below
459 the surface layer affected by these processes. The calculated flux of dissolved sulphate is 18.1
460 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station D, 4.3 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station B, 0.48 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station A,
461 and 1.26 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station WH (Table 1). These values correspond to rates of POC
462 mineralization of 36.3, 8.5, 1.0, and 2.5 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$, respectively.

463

464 Similar calculations can be realized based on ammonia fluxes in order to assess
465 mineralization processes that occur in buried sediments (Soetaert et al., 1996; Burdige and
466 Komada, 2013). Fluxes of NH_4^+ obtained (Table 1) are 4.49 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station D, 1.25
467 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station B, 0.18 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station A and 0.41 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$ at station
468 WH. Considering a typical C:N ratio of marine organic matter of 106:16 (Redfield et al.,
469 1963), these values correspond to POC mineralization rate of 29.7, 8.3, 1.2 and 2.7 $\mu\text{mol cm}^{-2}$
470 yr^{-1} , respectively. These values are close to organic carbon mineralization rates deduced from
471 sulphate profiles. This should not be considered as an indication that dissimilatory sulphate
reduction is the only process of N mineralization during anoxic diagenesis, because

472 methanogenesis produces ammonium as well. When sulphate is reduced with methane, one
473 methane reacts with one sulphate. As 16:53 ammonium is produced for one methane produced
474 during methanogenesis, and also for one sulphate consumed during sulphate reduction,
475 according to a Redfield composition of organic matter (C:N=106:16), the production of
476 ammonium relative to sulphate consumption remains the same whatever the process for
477 sulphate reduction (AOM or dissimilatory).

478 Considering that chemical fluxes and MAR are steady during the Holocene, it is
479 possible to calculate the loss of POC due to organic matter mineralization by anoxic processes
480 that consume sulphate. Calculated values are 0.058, 0.21, 0.16 and 0.30 mmol of mineralized
481 POC per gram of dry sediment, at stations D, B, A, and WH respectively, which represent
482 0.69, 2.6, 2.0 and 3.6 mgC g⁻¹. It corresponds to a decrease in POC concentration of 0.069%
483 (D), 0.26% (B), 0.2% (A) and 0.36% (WH) by sulphate reduction and methanogenesis. We
484 observe a decrease in POC concentration in the anoxic part of studied cores, although POC
485 loss is lower than that calculated above. This is probably because our long cores have only
486 sampled the upper part of the anoxic zone. More particularly, Kullenberg cores B, A, and WH
487 did not sample the deep sediment zone in which sulphate disappears. It appears in any case
488 that our results highlight the fact that the decrease in POC concentration in sediment cores
489 should not be attributed directly to paleo-oceanographic evolution of POC fluxes at the
490 sediment surface. Because diagenetic processes alter POC concentration, not only close to the
491 sediment surface (Mouret et al., 2010), but also at several meters depth, buried POC
492 represents only a transformed relict of POC exported to the sediment surface from the water
493 column.

494

495 **4.3. Secondary reactions**

496

497 4.3.1. Carbonate precipitation

498

499 The anoxic zone of marine sediments has been recognized as a site of carbonate
500 precipitation because sulphate reduction and anaerobic oxidation of methane produce
501 alkalinity (De Lange, 1986; Mucci et al., 2000; Berelson et al., 2005; Snyder et al., 2007).
502 Carbonate precipitation can be quantified using pore water Ca²⁺ profiles (Chatterjee et al.,
503 2001). At all studied sites, dissolved calcium concentrations decrease with depth, suggesting
504 that precipitation of secondary calcium carbonate may occur. Mean diffusive fluxes of
505 dissolved calcium estimated using Fick's first law are 3.34, 1.07, 0.24, and 1.60 μmol cm⁻² yr⁻¹

506 ¹ at stations D, B, A, and WH, respectively (Table 1), which corresponds respectively to
507 CaCO₃ precipitation rates of 0.334, 0.107, 0.024, and 0.160 mg cm⁻² yr⁻¹. At station B, the
508 mean mass accumulation rate is 40 mg cm⁻² yr⁻¹ and carbonate minerals represent about 20%
509 of sediments. Therefore, the rate of calcium carbonate sedimentation is 8 mg cm⁻² yr⁻¹.
510 Authigenic calcium carbonate linked to diagenetic processes represent 1.34% (0.107/8) of
511 total carbonate in anoxic sediments. Similar calculation indicates authigenic carbonate
512 contents of 0.4, 1.2, and 5.6% at stations D, A, and WH, respectively. These values are lower
513 than the estimate based on a compilation of measurements of the calcium concentration of
514 pore fluids collected at numerous seafloor sites around the globe. Authigenic carbonate
515 precipitation accounts for at least 10% of global carbonate accumulation (Sun and Turchyn,
516 2014). The proportions of authigenic calcium carbonate are low in the Bay of Biscay cores
517 mostly because they are diluted in an initial high biogenic CaCO₃ content. In some cores, such
518 as at station WH, the geochemical signature of fossilized calcium carbonate may be
519 significantly contaminated by new carbonates formed during diagenesis.

520 Manganese behaviour in anoxic sediments can be influenced by carbonate chemistry
521 (Mucci, 1988) through co-precipitation with calcium carbonates to form a rhombohedral
522 carbonate solid solution (Middelburg et al., 1987). Dissolved manganese profiles along the
523 Kullenberg cores show a decrease at the top of the anoxic zone of the sediments, from 10 to
524 50 cm depth. Concentrations of manganese extracted with HCl increase slightly with depth,
525 suggesting that dissolved Mn precipitate. At stations B, A, and WH, calculated downward
526 diffusive fluxes of dissolved manganese correspond to accumulation rates of authigenic
527 manganese of about 1 μmol g⁻¹ (from 0.82 to 1.25 μmol g⁻¹), which cannot be observed in the
528 Mn-HCl profiles because 1 μmol g⁻¹ is the error margin of the HCl extraction procedure.

529

530 4.3.2. Phosphorus behaviour

531

532 Dissolved inorganic P concentrations increase with depth in the studied cores,
533 suggesting that P included in organic matter is mineralized and released in pore water.
534 However, the N/P ratio, as deduced from the NH₄⁺/DIP ratio, shows non-constant profiles
535 along the cores. Values obtained at the bottom of the cores range between 50 and 200 (Fig. 5),
536 which is far above the Redfield ratio of 16 determined for marine organic matter (Redfield et
537 al., 1963). High N:P ratios may result from phosphate precipitation as an authigenic
538 particulate phase. Authigenic apatite or vivianite precipitation (Ruttenberg and Berner, 1993;
539 Dijkstra et al., 2018), or phosphorus adsorption on secondary carbonates (De Kanel and

540 Morse, 1978) are the main processes of particulate P formation in anoxic sediments. The
541 observed increase in P-HCl with depth (from 2 to 5 $\mu\text{mol.g}^{-1}$ depending on the station; Fig. 4)
542 points out that P authigenesis occurs here. Vivianite can be extracted with an ascorbate
543 solution (Anschutz and Deborde, 2016), but apart from the bottom of station D core, P-Asc
544 does not increase with depth, suggesting that P probably forms apatite or it co-precipitates
545 with calcium carbonates (Tribovillard et al., 2010). Authigenic vivianite may be formed in the
546 methane-rich sulphate-free layer of station D (Dijkstra et al., 2018). DIP precipitation is
547 deduced from high NH_4^+/DIP ratio. However, we observed no decrease in DIP with depth, but
548 an increase. This suggests that DIP precipitation rate is balanced by a higher rate of DIP
549 production. DIP that forms authigenic phases comes from a deep source, contrary to calcium
550 or manganese. This deep source is probably the anoxic mineralization of organic matter. DIP
551 can also be released into the sediment pore water after reductive dissolution of P-bearing iron
552 oxides by sulphide produced through sulphate reduction during diagenesis of buried
553 sediments.

554

555 **4.4. Anoxic diagenesis and fluxes to the ocean**

556

557 Major dissolved elements in sediment pore water, such as calcium, magnesium, and
558 potassium, show concentration gradient due to deep sediment diagenesis (e.g. Sayles and
559 Manheim, 1975 ; McDuff and Gieskes, 1976). Fluxes have been deduced from these gradients
560 and have been included in the mass balance of ocean chemistry (e.g. Sayles, 1979; Sun et al.
561 2016). Fluxes across the sediment-water interface of biogenic compounds, such as carbon,
562 nitrogen and phosphorus, have been measured or calculated from pore water profiles in deep
563 sea and coastal environments (Emerson and Hedges, 2003). Most of the studies on benthic
564 biogeochemistry have been conducted on sediments lying just below the sediment water
565 interface, since most of the organic matter is mineralized in the first centimetres of sediment.
566 Several studies also show that sediment diagenesis far below the sediment interface feeds the
567 surface sediment with nutrients (e.g. Schulz et al., 1994; Niewohner et al., 1998; März et al.,
568 2008; Chong et al., 2018). Our study allows us to quantify the N- NH_4 and DIP fluxes that
569 reach the sediment water interface for the 200-2000 m water depth part of the Landes Plateau.
570 This part of the Bay of Biscay (Fig. 1) extends over 6000 km^2 that is covered with muddy
571 sediment. Based on bathymetry mapping, we can consider that stations D, B, A, and WH are
572 representative of 2%, 10%, 34%, and 54% of the Landes Plateau area. The extrapolation of
573 the N- NH_4 fluxes (45, 12.5, 1.8, and 4 $\text{kmol km}^{-2} \text{yr}^{-1}$ at station D, B, A, and WH,

574 respectively) to the whole Landes Plateau area, allows estimating a total weighted average
575 flux of about 30 Mmol yr⁻¹ N-NH₄. This value is low compared to N-NO₃ fluxes issuing from
576 rivers that flows into the southern Bay of Biscay. For example, the flux of N-NO₃ from the
577 Gironde estuary is 2700 Mmol yr⁻¹ (Anschutz et al., 2016). Nevertheless, the calculated
578 benthic flux compares to the flux of N-NO₃ of the smaller Leyre River, which drains 2000
579 km² of forest and crops. A similar calculation has been done for DIP. The flux of DIP
580 calculated from the concentration gradient is 95, 98, 0, and 25 mol km² yr⁻¹ for station D, B,
581 A, and WH, respectively, which gives an extrapolated flux of 151 kmol yr⁻¹ for the Landes
582 Plateau.

583

584 **5. Conclusion**

585

586 Profiles of dissolved compounds involved during organic matter mineralization have
587 been obtained from interface and Kullenberg cores at four sites of the Bay of Biscay. They
588 indicate that biogeochemical processes of organic matter degradation occur in the buried
589 sediments, all along the Holocene sequence, and beyond, through sulphate reduction and
590 methane genesis. These processes favour the precipitation of secondary calcium carbonates
591 but also authigenic forms associated to Mn and phosphorus. Fossilization of some
592 geochemical proxies like POC, carbonates, phosphorus, or manganese, is a long-term process.
593 Diagenetic reactions, which modifying these proxies, must be quantified in order to
594 distinguish in a sedimentary record the part resulting from post-deposition transformations.
595 More particularly, our results show that the decrease in POC concentration in sediment cores
596 should not be directly attributed to paleo-oceanographic evolution of POC fluxes at the
597 sediment surface. We show also that coatings of authigenic calcium carbonate may represent
598 several percent of new carbonate relative to initial carbonate content, with a geochemical and
599 isotopic signature, which may be very different of biogenic material.

600 Contribution of early diagenesis to POC loss and CaCO₃ authigenesis has to be
601 estimated in paleo-oceanographic studies. Our study is based an extensive data set on 15
602 chemical parameters measured along four sediment cores. Such long and fastidious work
603 cannot always be done on long cores dedicated to paleo-oceanographic studies. Our results,
604 however, suggest us to encourage the paleo-oceanographic community to follow these
605 recommendations: bring a small bench top centrifuge during cruises to extract pore waters. In
606 each deep-sea core collect about 20 ml sediment in a centrifuge tube at regular interval (e.g

607 every 50 cm for a 10 m long core, or a better vertical resolution if possible), extract pore
608 water and after filtration with a syringe filter, keep the water in a fridge. This will give enough
609 pore water to obtain profiles of dissolved calcium, sulphate and ammonium. These three
610 parameters will allow to locate the sulphate-methane transition zone and to quantify
611 authigenic carbonate formation and deep sediment organic matter mineralization.

612

613

614

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616

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625

626

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906 **Figure captions**

907

908 Figure 1: Bathymetric map of the southern part of the Bay of Biscay and location of stations
909 (St) where sediment cores were sampled

910

911 Figure 2: Vertical profiles of sediment properties at the 4 studied stations: porosity (%),
912 median grain size (D50 in μm), ^{14}C dating in cores B, A, and WH in calendar years BP, and
913 $^{210}\text{Pb}_{\text{xs}}$ and ^{137}Cs profiles in gravity and interface cores of station D.

914

915 Figure 3: Vertical profiles of particulate organic carbon concentration (POC in dry weight %),
916 CaCO_3 in dw% calculated from particulate inorganic carbon concentration, and total
917 particulate sulphur (TS, in $\mu\text{mol g}^{-1}$) at the 4 stations. Profiles have been drawn from data
918 obtained on long gravity cores, and from averaged profiles obtained from interface cores
919 (surf) collected between 1998 and 2006.

920

921 Figure 4 : Vertical profiles of particulate P, Fe, and Mn obtained after leaching with an
922 ascorbate (Asc) solution and a 1-N HCl solution. Profiles have been drawn from data obtained
923 on long gravity cores, and from averaged profiles obtained from interface cores (surf)
924 collected between 1998 and 2006. Note the change in concentration scale for Fe and Mn at
925 station WH.

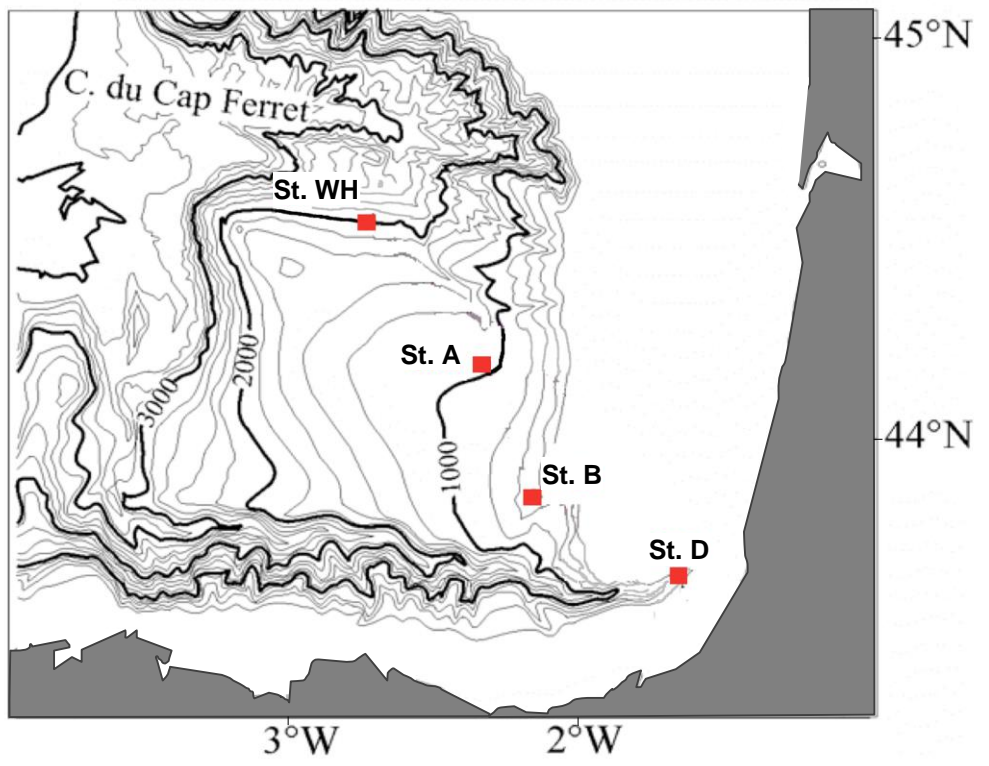
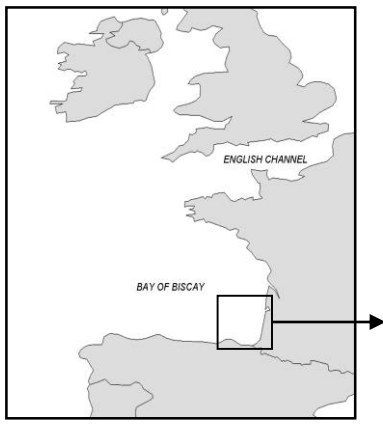
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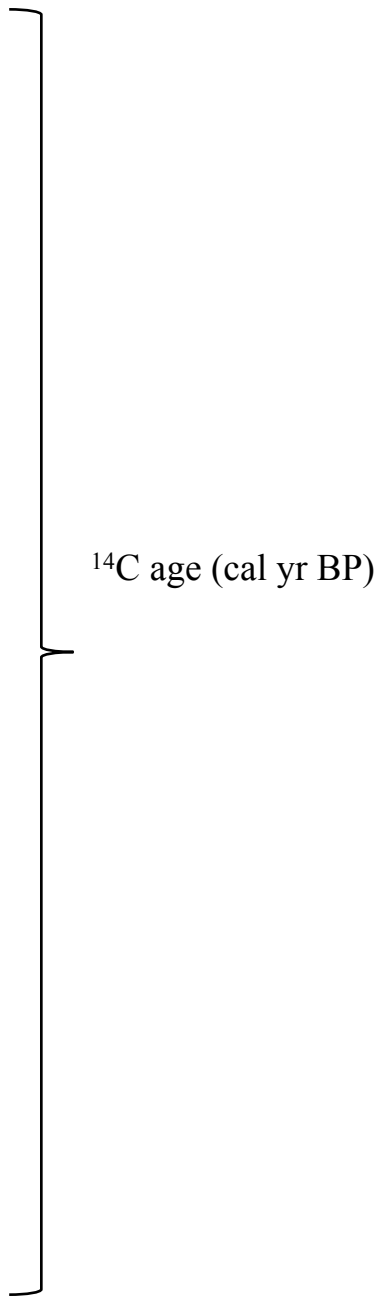
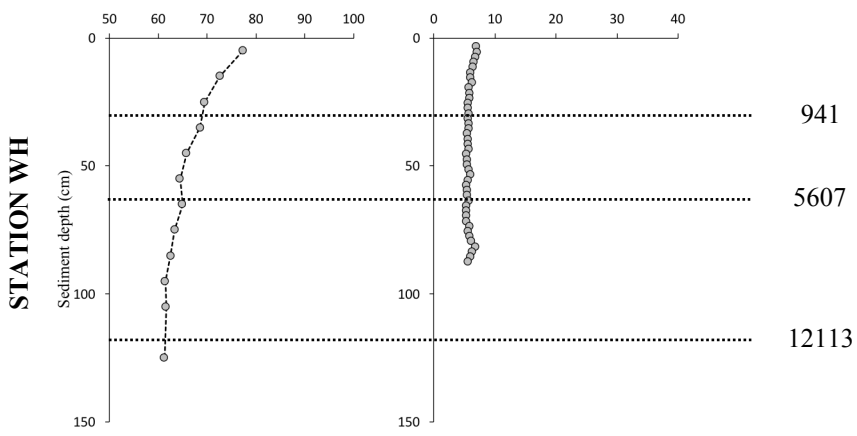
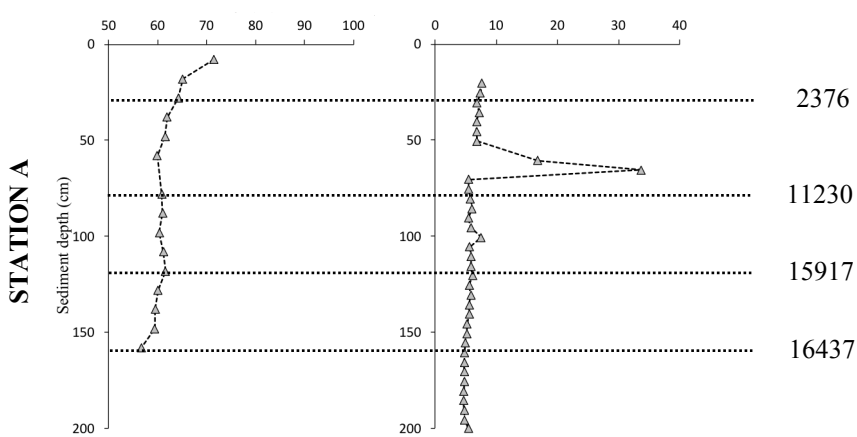
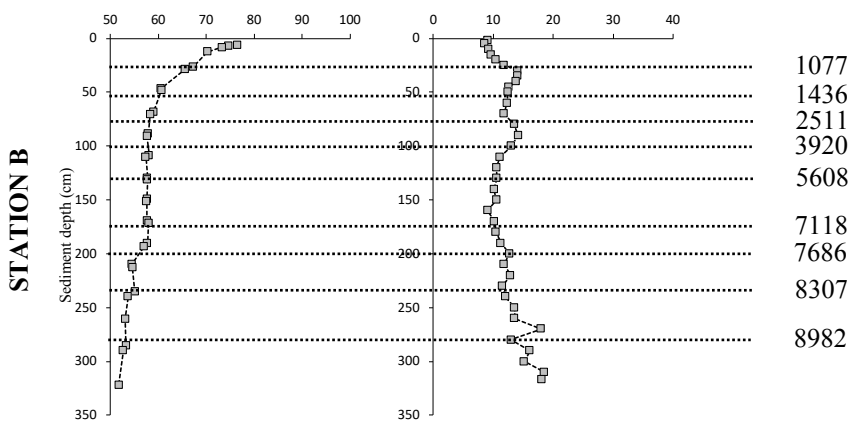
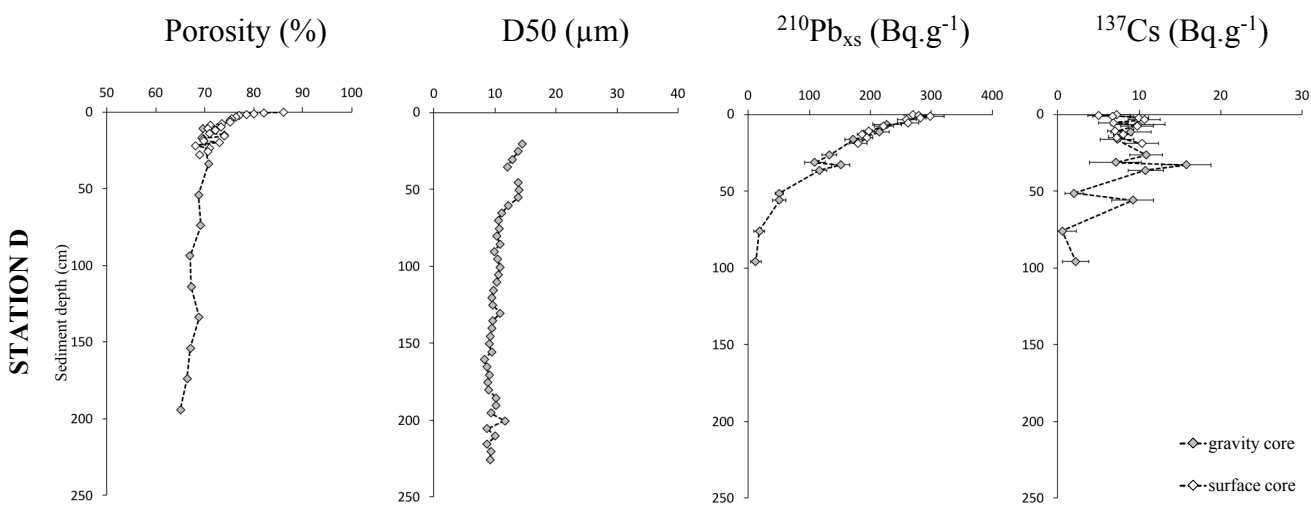
927 Figure 5 : Vertical profiles of dissolved nitrate, ammonium, inorganic phosphorus (DIP),
928 NH_4^+/DIP ratio, methane, Fe and Mn, sulphate, calcium, and dissolved inorganic carbon
929 (DIC) in sediment core pore waters. Profiles have been drawn from data obtained on long
930 gravity cores, and from averaged profiles obtained from interface cores (surf) collected
931 between 1998 and 2006.

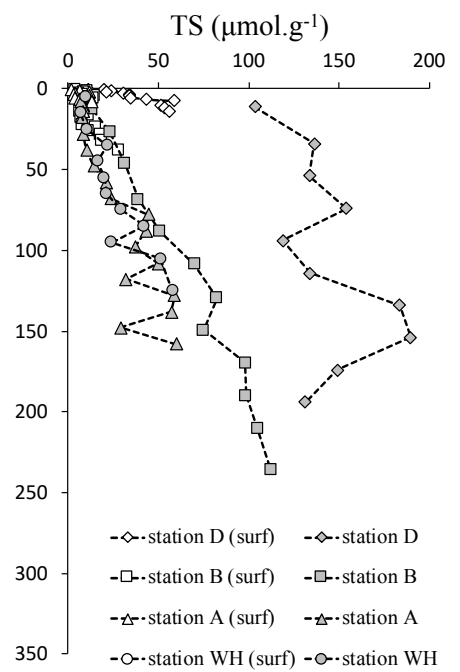
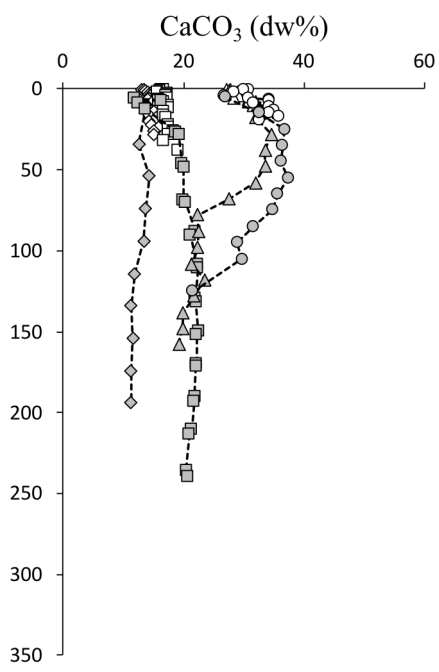
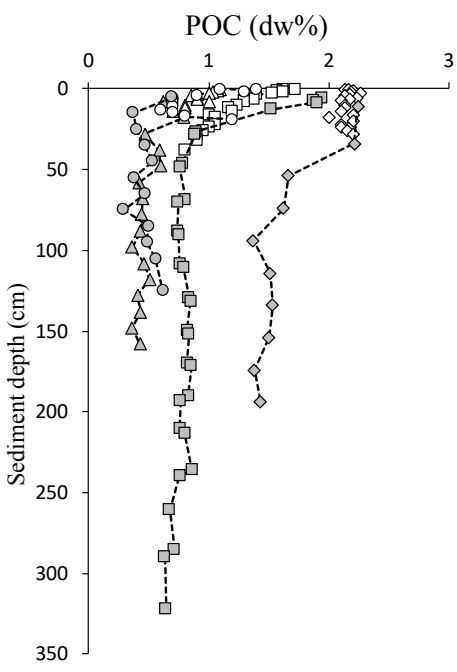
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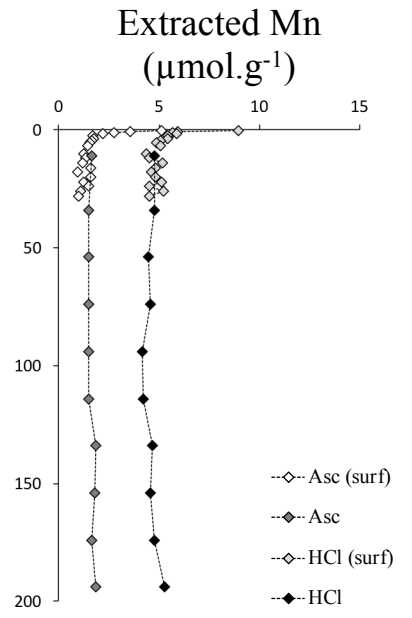
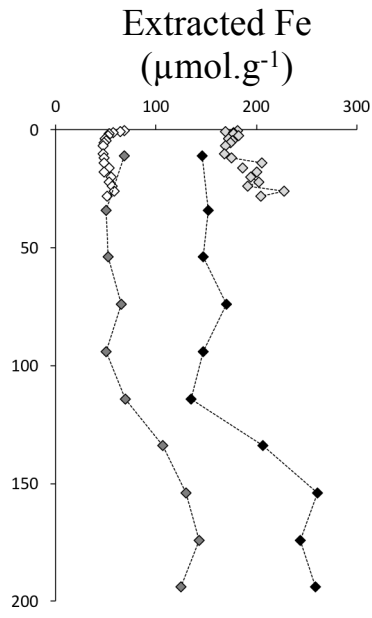
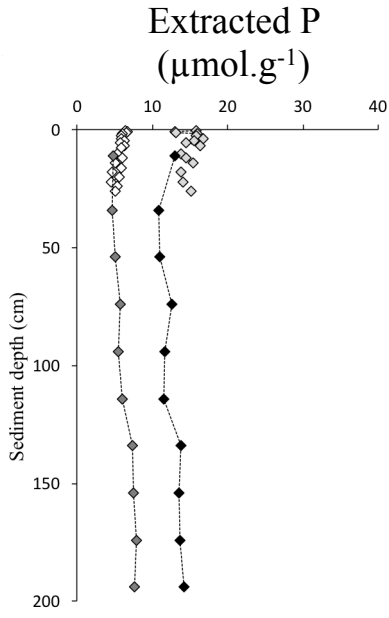
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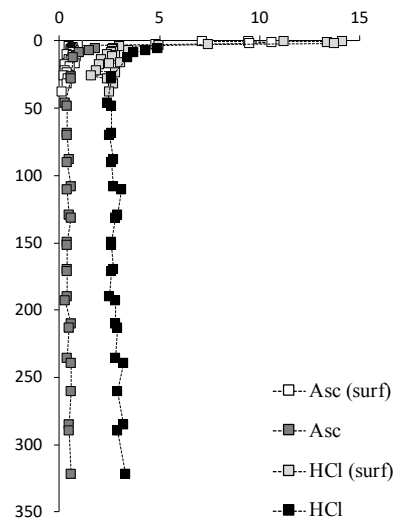
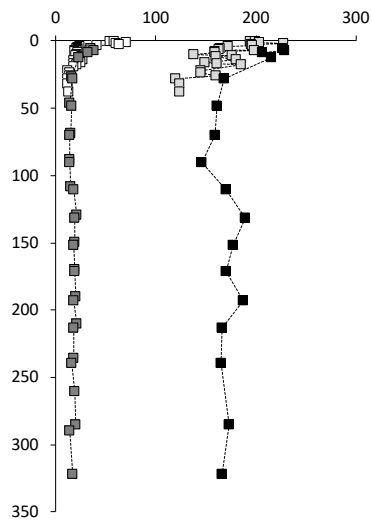
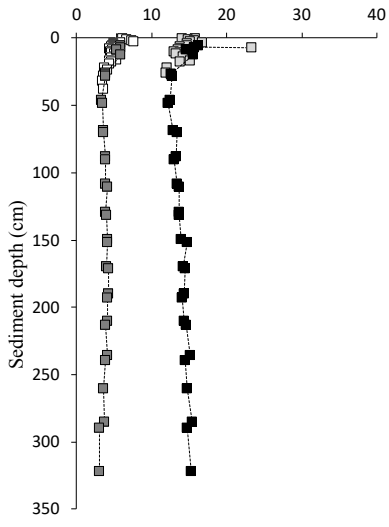




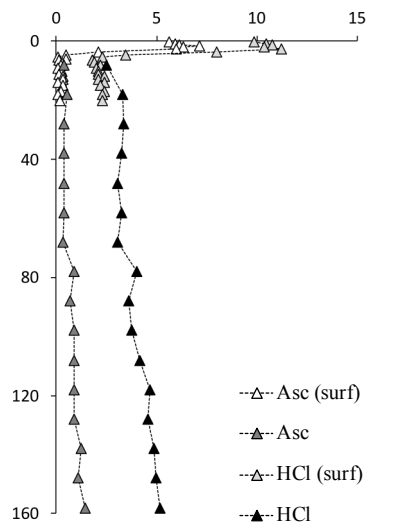
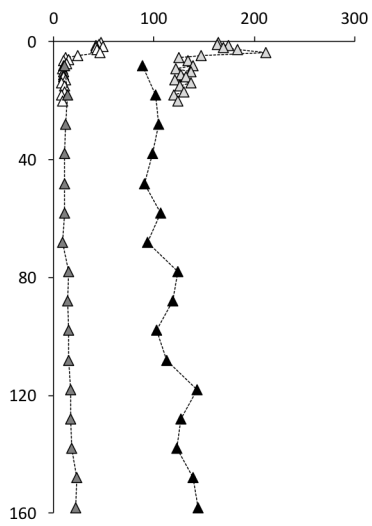
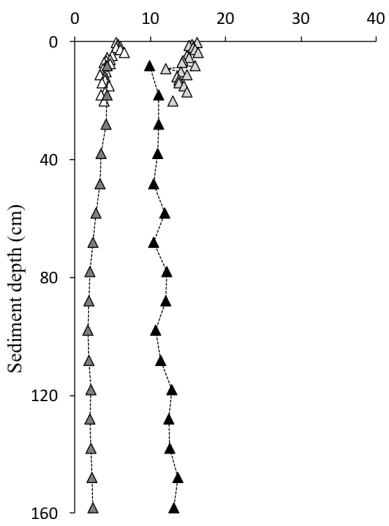
STATION D



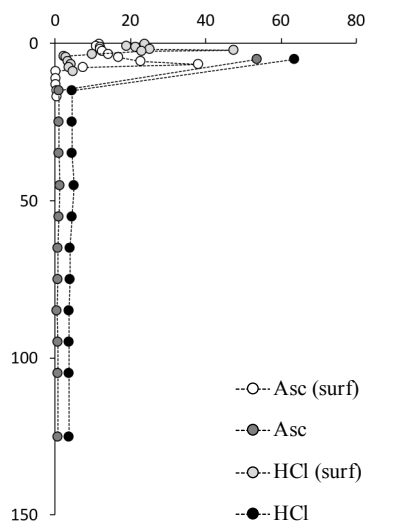
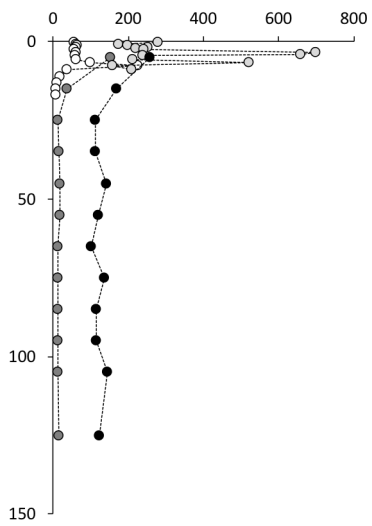
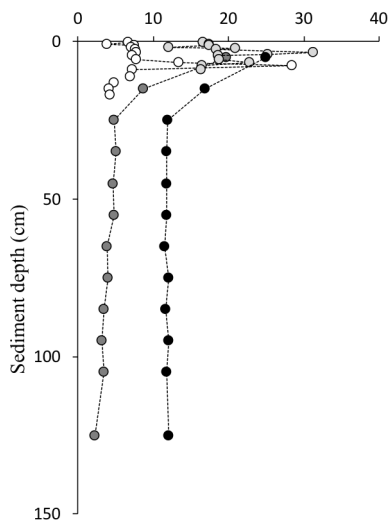
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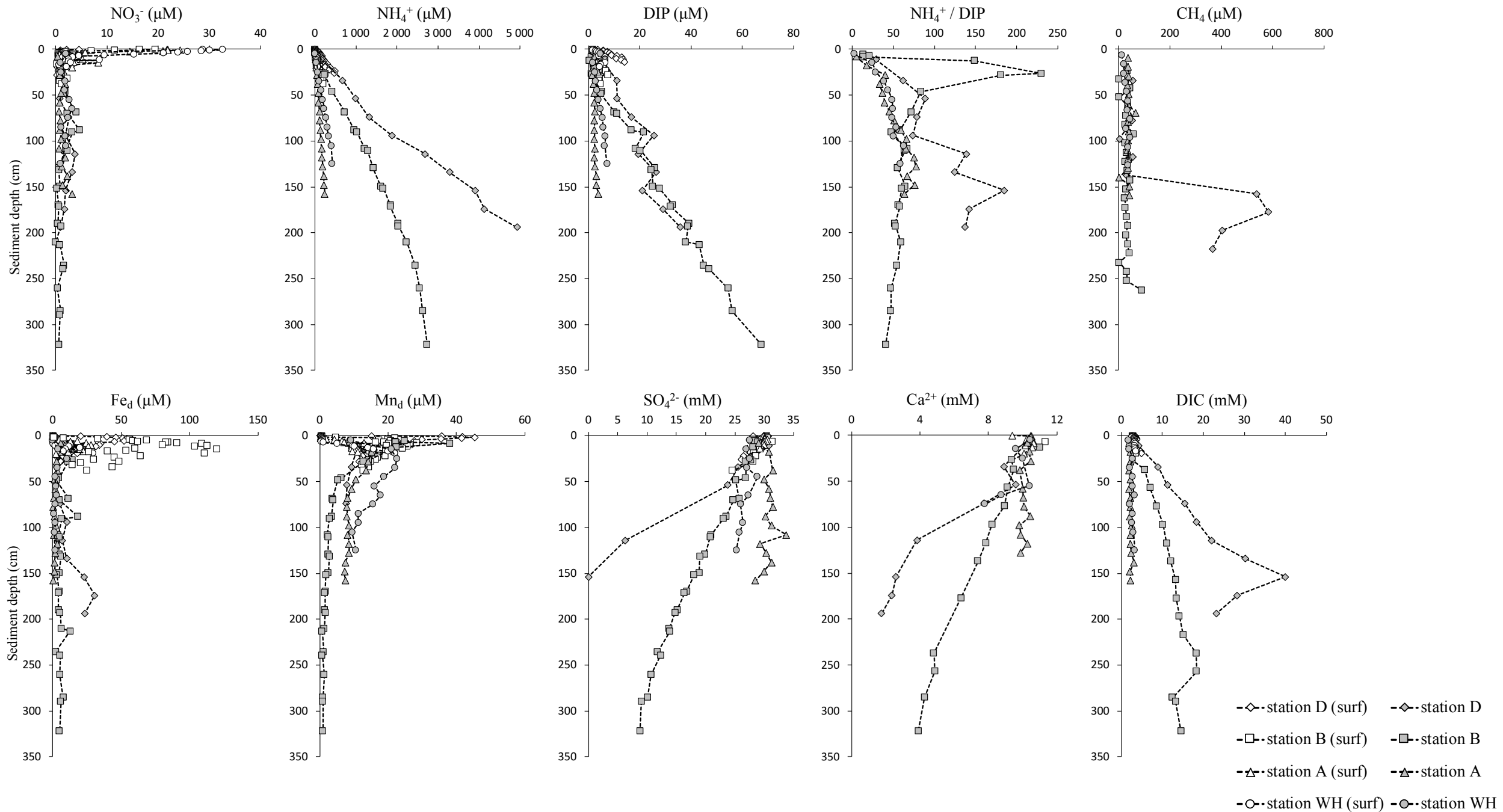


STATION A



STATION WH





1 Table 1 : Diffusive fluxes (in $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$) of sulphate, ammonium, calcium, and phosphate
 2 dissolved in sediment core pore waters. D_s (in $\text{cm}^2 \text{ s}^{-1}$) is the diffusion coefficient calculated
 3 from tracer diffusion coefficient in seawater after Schulz and Zabel (2006) and porosity
 4 according to [Boudreau \(1996\)](#). The diffusive coefficient of HPO_4^{2-} has been chosen to
 5 represent the flux of dissolved inorganic phosphorus.
 6

Station	Depth (m)	T (°C)	Porosity	SO_4^{2-}		NH_4^+		Ca^{2+}		HPO_4^{2-}	
				D_s	flux	D_s	flux	D_s	flux	D_s	flux
D	140	12	0.67	4.00E-10	18.1	7.56E-10	4.49	3.01E-10	3.34	2.82E-10	0.0095
B	550	11	0.58	3.35E-10	4.26	6.34E-10	1.25	2.51E-10	1.07	2.35E-10	0.0098
A	1000	10	0.61	3.41E-10	0.48	6.49E-10	0.18	2.56E-10	0.24	2.39E-10	\
WH	2000	4	0.63	2.86E-10	1.26	5.51E-10	0.41	2.13E-10	1.60	1.96E-10	0.0025

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