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Impact of Oyster Farming on Diagenetic Processes and the Phosphorus Cycle in Two Estuaries (Brittany, France)

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Abstract:

This study aims to compare the impact of oyster cultures on diagenetic processes and the phosphorus cycle in the sediments of the Aber Benoît and the Rivière d'Auray, estuary of Brittany, France. Our results showed clear evidence of the seasonal impact of oyster cultures on sediment characteristics (grain size and organic matter parameters) and the phosphorus cycle, especially in the Aber Benoît. At this site, seasonal variations in sulfide and Fe concentrations in pore waters, as well as Fe–P concentrations in the solid phase, highlighted a shift from a system governed by iron reduction (Reference) to a system governed by sulfate reduction (beneath oyster). This could be partly explained by the increase in labile organic matter (i.e., biodeposits) beneath oysters, whose mineralization by sulfate led to high sulfide concentrations in pore waters (up to 4,475 µmol l^{-1}). In turn, sulfide caused an enhanced release of phosphate in the summer, as adsorption sites for phosphate decreased through the formation of iron–sulfide compounds (FeS and FeS_2). In the Aber Benoît, dissolved Fe/PO_4 ratios could be used as an indicator of phosphate release into oxic water. Low Fe/PO_4 ratios in the summer indicated higher effluxes of phosphate toward the water column (up to 47 µmol m^{-2} h^{-1}). At other periods, Fe/PO_4 ratios higher than 2 mol/mol indicated very low phosphate fluxes. In contrast, in the Rivière d'Auray, the occurrence of macroalgae, stranding regularly all over the site, clearly masked the impact of oyster cultures on sediment properties and the phosphorus cycle and made the use of Fe/PO_4 ratios more difficult in terms of indicators of phosphate release.

Keywords: Sediment ; Phosphorus ; Sulfide ; Dissolved Fe/P ratios ; Labile organic matter ; Oyster cultures

1 Introduction

Marine farming in France is currently dominated to a great extent by oyster farming. French oyster production, mainly the species Crassostrea gigas, represents 130,000 tonnes per year with a turnover close to 25 million euros per year, making France the leading European producer. However, summer mortalities of C. gigas have been observed for several years along the French coast. An initial understanding of the complex interactions between oysters, environment, and pathogens was obtained during an interdisciplinary network, the MOREST project (2001–2005) on summer mortality events of C. gigas oysters in France (Samain and McCombie *2007*). This project highlighted the involvement of multiple factors, including the genetic and physiological status of the oysters; the occurrence of pathogens and environmental factors such as temperature, high trophic conditions, which control reproduction intensity and susceptibility to bacterial infection; and sediment proximity (Samain and McCombie *2007*). As an example of this last factor, in the Marennes-Oléron

Bay, the daily mortality rates of “on-bottom” oysters, reared directly on intertidal sediments, were significantly higher than those of “off-bottom” oysters reared on trestles (Soletchnik et al., 2005 ; Gagnaire et al., 2006). This potential involvement of sediment in the occurrence of mortalities could be an indirect consequence of the impact of oyster farming activities on the sediment itself. The benthic effects of oyster farming, where no excess food is supplied seem to be much less serious than those of caged fish farming (Matijevic et al., 2008). However, several studies have demonstrated how bottom sediments below the oyster racks were highly polluted by organic matter due to the biodeposition of faeces and pseudofaeces, and silt sedimentation (Nugues et al., 1996 ; Mallet et al. 2006). Under these conditions high mineralization rates can occur, changing biogeochemical cycling to reactions that promote the release of large quantities of inorganic nutrients into the water column (Berelson et al., 1998). In fact, when high mineralization rates occur, oxygen becomes depleted and sulphate reduction is stimulated leading to increased sulfide and ammonia production, which are known to be toxic to macro-organisms. In addition, the occurrence of anoxic conditions may contribute to an increase in phosphate liberation through the dissolution of Fe(III)-bound-P (Andrieux-Loyer and Aminot, 2001 ; Andrieux-Loyer et al., 2008 ; Anschutz et al., 1998 ; Krom and Berner, 1980, 1981 ; Sundby et al., 1992). This additional released P may significantly increase the biologically available pool of P in the water, thus modifying the trophic resource.

The effect of shellfish farming has especially been studied concerning nitrogen dynamics (Pietros and Rice, 2003 ; Mazouni, 2004 ; Nizzoli et al., 2006). However, relatively little is known of the impact of oyster cultures on mineralization processes and nutrient dynamics regarding the phosphorus cycle and including both the speciation of particulate phosphorus forms and dissolved nutrient data (Anschutz et al., 2007). Most studies on the impact of oyster cultures on nutrient cycles have mainly focused on nutrient fluxes (Gaertner-Mazouni et al., 2012 ; Hyun et al., 2013).

This study aims to assess the effects of oyster cultures on sediment characteristics and nutrient fluxes by focusing on the phosphorus cycle and how these effects differ according to seasons and sites. This study also provides important data for drawing up oyster aquaculture models, which do not yet adequately describe the effects of shellfish farms on benthic nutrient fluxes (Giles et al., 2006).

II. Materials and methods

II. 1. Site description

Sampling was conducted in two French estuaries where oyster farming is highly developed (figure 1 A and B) : (1) the downstream part of the Aber Benoît (4°36'W and 47°36'N) and (2) an oyster culture site (Fort Espagnol) near the mouth of the Rivière d'Auray (2°58'W and 47°36'N).

The Aber Benoît (figure 1 $B_{1,}$ table 1) is an estuary 31 km in length, with a catchment area of 140 km^2 , situated in the Northwest of Finistère (Brittany). The average water flow in spring is 0.418 m^3 s^{-1} but this site is subjected to strong seawater currents (up to 1.3 m s^{-1}) due to the high tidal amplitude, and salinity ranges from 24 to 34 (PSS78). Depth at zero tide is 14 m. Human activities, which mainly center on animal husbandry, lead to moderate discharges of organic matter, nitrate-rich fertilizers and sometimes pesticides into Aber Benoît. The total oyster area (250 ha) is located within Aber Benoît (38 ha) and Aber Wrac'h and between them. Before 2008, no summer mortality occurred and the temperatures never reached 19 °C.

The estuarine area of Auray (figure 1 $B_{2,}$ table 1) is 56.4 km in length and represents the western part of the Gulf of Morbihan in South Brittany. It is influenced by human activities, mainly agriculture, in a catchment area of 800 km^2 around two principal rivers, the Loch and the Sal. These rivers flow into Rivière d'Auray with an average flow of 2.99 m^3 s^{-1} for the Loch and about half this for the Sal. The tidal flux causes a renewal of 50 % of the Gulf's water every 10 days (20 tides) and produces a current up to 0.4 m s^{-1}. In the downstream part of Rivière d'Auray, which is used for oyster farming (1635 ha), salinity varies from 27 to 35 (PSS78). Depth at zero tide is 20 m. Oyster mortality has occurred almost every year since the phenomenon began, notably because the temperatures exceed 19 °C in summer.

Both sites are well-suited for breeding oysters due to the presence of phytoplankton blooms.

The sediment of Aber Benoît is sandy mud with a deep grey colour, while the Rivière d'Auray sediment is black sandymud.

In each site, experiments were performed, over a seasonal cycle, at a station under the influence of oyster cultures (Oyster) compared to processes at a station outside their direct influence (Reference, 30 m away from Oysters**).** However, as all Rivière d'Auray was subjected to green macroalgal growths, a reference site without these macroalgae could not be found.

Oyster and Reference sites were subjected to 60-70 % immersion, i.e., emergent at low tide during spring tide. Pacific oysters Crassostrea Gigas were reared in bags placed on 50 cm high racks on each sample site.

II. 2. Sampling

In each site, sediment samples were collected on a monthly basis from July to September 2007 and in March, May and June 2008. Sediment and its overlying water were collected by a hand corer using PVC cores (id = 9 cm; h = 30 cm), as described in Mudroch and Azcue (1995). Any disturbance of the sediment-water interface was carefully avoided. Triplicate cores were taken at each station. This study was carried out during similar hydrodynamic conditions (moderate spring tide, ebb tide). Overlying physical-chemical water properties are illustrated in figure 2.

II. 3. Overlying and pore water treatments

All overlying and pore water treatments were performed at the sampling site. An aliquot of overlying water was collected immediately after core recovery for further nutrient analyses. Temperature and Salinity (expressed on the PSS78 scale) in overlying waters were measured with a WTW portable meter (LF 320). High resolution vertical profiling of dissolved O_2 was then carried out both in overlying and pore waters using a miniaturized Clark-type oxygen sensor (Unisense OX500) coupled with a picoammeter (Unisense PA2000) and a micromanipulator (Unisense MM33). The in-situ temperature was maintained by using an insulating device.

Subsequently, the core used for O_2 profiling was sliced into six horizontal layers up to a total depth of 8 cm (0.5 cm for the top 1 cm, 1 cm up to 3 cm, 2 cm up to 5 cm, 3 cm below) within 30 min. Two other cores were sliced up to 2 cm for diffusive fluxes statistical treatments. For every level, a sub-sample was centrifuged in a Whatman VectaSpin 20TM centrifuge tube filter (0.45 µm) under inert atmosphere (N_2) at 3075 g and 4 °C for 20 min in order to collect pore waters.

An aliquot of pore water was diluted tenfold in 0.02 M hydrochloric acid and maintained at 4 °C for Fe^{2+} and Mn^{2+} analysis. Another aliquot was diluted fifty fold in a 4.6 mM zinc acetate solution for hydrogen sulfide analysis. The remaining pore water was acidified at pH ~ 2 and frozen for subsequent nutrient analysis.

II. 4. Sediment treatments

An aliquot of the wet sediment of known volume and weight was dried at 60 °C (5 days) and the weight loss was used to calculate porosity (Berner, 1980). Another sample was maintained at 4 °C for less than 15 days for sediment grain size. An aliquot of the sediment remaining after collection of pore water was frozen at –25 °C for subsequent Chlorophyll a (Chl a) and Phaeopigment analysis. Another aliquot was also frozen at –25 °C, then freeze-dried, for the subsequent organic Carbon (Orga-C), total N, and phosphorus forms analysis.

Sequential extraction of phosphorus pools and analysis

The major reservoirs of sedimentary P -Adsorbed and iron-oxide bound P (Fe-P) and Authigenic Calcium bound P (Auth-Ca-P)- were determined using the widespread sequential method of Ruttenberg (1992), as modified by Andrieux-Loyer *et al.*, 2008. The main features are presented in table 2. In this study, we omitted citrate in the first step as it was shown to render a part of the calcium-bound phosphate soluble (Psenner, 1988). In addition, the $MgCl_2$ and H_2O washes were omitted in step I. These were originally used to avoid the secondary sorption of P on the residual solid surfaces during the extractions. This process was shown to be insignificant in the dithionite extraction (Ruttenberg, 1992 ; Slomp, 1996 a).

Organic P (Orga-P) was determined nonsequentially as the difference between 1 M HCl extractable P before (24 h : inorganic P) and after the ignition of the sediment (550 °C, 4 h; Total P ; Aspila *et al.*, 1976). The sedimentary inorganic carbon was removed with phosphoric acid (Cauwet, 1975) before Orga-C analysis.

II. 5. Analytical procedures

The analysis of sediment grain size was performed using LS 200 Beckman Coulter laser granulometry. Organic C (Orga-C) and total N were measured using a vario EL-III CN elemental analyser. Chl a and Phaeopigments were determined according to Lorenzen (1967) as modified by Aminot and Kerouel (2004).

The pore water was diluted tenfold after thawing, then analyzed using segmented flow analysis (SFA) for phosphate, nitrate and ammonium (Aminot et al., 2009). Phosphorus form extracts were also diluted tenfold and dithionite extracts were additionally acidified with H_2SO_4 (Jensen and Thamdrup, 1993), then bubbled with pure O_2 (30 ml min^{-1}) for one minute to transform S in SO_4, which may interfere in colorimetric methods and phosphate determination in the extracts. The method of standard additions was used to check for potential interferences and to correct the results accordingly.

Fe^{2+} in pore water was measured with the ferrozine method (Sarradin *et al.*, 2005) and Mn^{2+} with the leuco-malachite green method (Resing and Mottl, 1992), both adapted for SFA.

Hydrogen sulfide (H_2S, HS^-, S^{2-}) was measured using the colorimetric methylene blue method according to Fonselius *et al.*, 1999.

The analytical precision of the determinations was better than 2 %.

II. 6. Calculation of diffusive fluxes

Diffusive fluxes were calculated using the first Fick's law adapted for sediments (Berner, 1980): $\mathrm{Fd} = -\phi \times \mathrm{Ds} \times (\frac{\mathrm{dC}}{\mathrm{dz}})$ (1), where Fd is the rate of efflux (µmol m^{-2} d^{-1}), Φ is the sediment porosity (dimensionless) of the upper sediment sample, Ds is the bulk diffusion coefficient (m^{-2} d^{-1}) and dC/dz is the concentration gradient at sediment-water interface for phosphate and ammonium (µmol m^{-4}). For HPO_4^{2-} and NH_4^+, dC/dz was calculated from linear regression on the concentration values at bottom water and just below the interface (table 3). For HS^-, the concentration gradient was calculated for the depth interval with the greatest concentration gradient change (table 3), with corresponding porosity (Sahling et al., 2002). Consequently, these sulfide fluxes represented the maximum of the ascendant sulfide fluxes in the sediment. Ds was corrected for tortuosity, *i.e.*, $D_s = \frac{D_0}{\theta^2}$, where θ is the tortuosity (dimensionless), D_0 is the diffusion coefficient in water for HPO_4^{2-}, NH_4^+ or HS^- (m^2 d^{-1}). The diffusion coefficient in water (D_0) was corrected for the in situ bottom water temperatures (Li and Gregory, 1974) and the value of θ was assumed to be equal to $\sqrt{1 - 2 \times \ln \varphi}$ (Boudreau, 1996).

II.8 Data processing

Surfer® software (version 8) was used to interpolate measured values and create contour maps for each measured solid and dissolved parameter. The gridding methods in Surfer uses weighted average interpolation algorithms. Kriging, used in this study, is the default gridding method because it generates the best overall interpretation of most data sets.

The normality of data sets was first assessed with the Shapiro & Wilk test (*www.anastats.fr)*. Speerman or Bravais-Pearson tests were used to evaluate relationships between variables (Xlstat). Mann and Whitney tests were performed to determine the significant differences of biogeochemical parameters between the Reference and Oyster stations at each study period (*www.anastats.fr)*. For all tests, values were considered significant at $p < 0.01$.

III. Results

III.1. Solid fraction

III.1.1. Sediment characteristics (granulometry, porosity, Carbon, Nitrogen and Chlorophyll a)

Sediment characteristics of surficial sediments (in the top 3 cm) are presented in table 4 and in table 5 in Appendix. Sediments were all sandy muds both in the Aber Benoît and in the Rivière d'Auray (Characterization of Larsonneur, 1971). Nevertheless, surficial sediments in the Aber Benoît always presented lower proportions of lutites (< 62.5 µm) than those in the Rivière d'Auray, both at the Reference and under Oysters (table 4). In the Aber Benoît, proportions of lutites (and the lowest median size) were always significantly higher beneath Oysters compared to the Reference (Mann and Whitney ; $n = 6$; $p < 0.01$), whereas no differences appeared in rivière d'Auray ($n = 6$; $p < 0.01$). Coefficients of variations in the Aber Benoît (8 % under racks ; 22 % outside racks) and in the Rivière d'Auray (7 % under rack ; 8 % at the Reference) indicated the relatively stable grain-size nature of surficial sediments at each station over time.

The surficial porosities were lower in the Aber Benoît than in the Rivière d'Auray (table 4). However, at both areas, differences between Reference and Oyster sites were not significant at each study period (Mann-Whitney tests ; $n= 6$; $p < 0.01$).

The vertical distributions of Orga-C (figure 3) and Total N (not shown) generally displayed a decrease or almost constant concentrations with depth, according to the season and the location. However, in the Aber Benoît in May and June, under Oysters, a significant increase in concentrations occurred respectively at 2-3 cm depth and at 5-7 cm depth (Orga-C > 2100-2700 µmol g^{-1} ; Total N: > 400 µmol g^{-1}). At the Reference, concentrations only increased in May in surficial sediments (Orga-C > 1200 µmol g^{-1} ; Total N > 200 µmol g^{-1}). In the Rivière d'Auray, seasonal variations occurred both under Oysters and at the Reference and the highest surficial concentrations (~2700 µmol g^{-1} in Orga-C ; ~ 500 µmol g^{-1} in Total N) were always observed in May and August.

Orga-C/total N (C/N) ratios (figure 4) varied from around 5.6 to 9.6 over the study period (Aber Benoît and Rivière d'Auray). At both sites, C/N ratios increased from March (6.1 ± 0.5) to Summer (9.0 ± 0.6 in the Aber Benoît and 9.4 ± 0.2 in the Rivière d'Auray).

Orga-C/Orga-P (C/P) ratios (figure 4) were more variable further down the core, generally increasing with depth. They also increased from March (about 230 ± 20 under Oysters in the Aber Benoît and 230 ± 154 under Oysters in the Rivière d'Auray) to June (393 ± 111 in the Aber Benoît at the Reference) or to July (724 ± 222 in the Rivière d'Auray under Oysters). There were no significant differences in C/N and C/P ratios between Reference and Oyster sites.

Chl a concentrations (figure 3), in the Aber Benoît, under Oysters, were characterized by two maxima (May, 50 µg g^{-1} in surficial layers ; June, 40 µg g^{-1} at 6 cm depth). At the Reference, concentrations rarely exceeded 10-20 µg g^{-1}. In the Rivière d'Auray, both under Oysters and at the Reference, two maxima also occurred, respectively in May and August (up to 70 µg g^{-1}) and in March and May (up to 80 µg g^{-1}).

Phaeopigment profiles (figure 3) displayed the same patterns than Chl a profiles but with concentrations up to 120 µg g^{-1} (Aber Benoît, under Oysters) and up to 211 µg g^{-1} (Rivière d'Auray, Reference).

III.1.2. P forms

In the Aber Benoît, the depth profiles showed differences between Reference and Oyters sites (figure 5 and table 5 in Appendix). In contrast, no marked differences appeared in the Rivière d'Auray (figure 5). By and large, Tot-P concentrations generally decreased with depth (not shown). In the Aber Benoît, under Oysters, Tot-

P concentrations were characterized by two maxima, the first one in May (24 µmol g^{-1} at 2.5 cm depth), the second in June in deeper layers (24 µmol g^{-1} at 6 cm depth). At the Reference, concentrations only significantly increased in May (20 µmol g^{-1} at 1 cm depth). In the rivière d'Auray, two maxima occurred in surficial sediments both under Oysters (about 24 µmol g^{-1} in May and August) and at Reference (20-26 µmol g^{-1} in March and September). Apart from these maxima, concentrations ranged from 10 to 15 µmol g^{-1}. Total P distributions were largely accounted for by Orga-P and Fe-P which globally showed the same patterns and to a lesser extent by Authigenic Ca-P.

In both areas, Fe-P mean concentrations were close to 2 µmol g^{-1}. In the Aber Benoît, under Oyters, concentrations reached about 5 µmol g^{-1} in May and June (2-6 cm depth). At the Reference, there was no significant increase. In the Rivière d'Auray, under Oysters, Fe-P concentrations in surficial sediments, showed a first increase in May and a second at the end of August (up to 11 µmol g^{-1}). At the Reference, the first maximum occurred in March (8.8 µmol g^{-1} at 0.5 cm depth) and the second in August (5.7 µmol g^{-1} at 2.5 cm depth). This phosphorus form represents 10 to 20 % of the total phosphorus in the Aber Benoît and 10-30 % of Total P in the Rivière d'Auray. No significant variations in proportions could be observed whatever the investigated area and site.

In the Aber Benoît, under Oysters, Orga-P patterns were characterized by an increase in concentrations both in May (12 µmol g^{-1} at 2.5 cm depth) and June (9.4 µmol g^{-1} at 6 cm depth). At the Reference, concentrations only increased in March and May in surficial sediments (up to 7.4 µmol g^{-1}). In the Rivière d'Auray, under Oyters, two maxima (up to 11.5 µmol g^{-1}) occurred in surficial sediments in May and August, whereas at the Reference, concentrations increased especially in May and at the end of September. Owing to the relatively wide concentration range (0-12 µmol g^{-1}) -according to the location and the season- the Orga-P proportions in relation to total P were relatively variable (15-30 % on average in the Aber Benoît ; 20-45 % on average in the Rivière d'Auray). No significant trend could be highlighted between Reference and Oyster sites, either in the Aber Benoît or in the Rivière d'Auray.

By and large, almost constant Auth-Ca-P concentrations occurred in the Rivière d'Auray (2-3 µmol g^{-1}). In contrast, in the Aber Benoît, two concentration maxima (4- 6 µmol g^{-1}) were observed both beneath Oysters and Reference, in May, June or July. Auth-Ca-P accounted for 10 to 18 % and 12 to 23 % of total P respectively in the Aber Benoît and in the Rivière d'Auray. The proportions of Auth-Ca-P did not display any effects of oyster cultures.

III.2. Pore water profiles

III.2.1. Redox sensitive species (O_2, NO_3^-, Fe^{2+} and Mn^{2+}, HS^-)

In the Aber Benoît, under Oysters, oxygen concentrations in the bottom waters (figure 6) varied from 235 µmol l^{-1} (July 3th) to about 300 µmol l^{-1} (June) over the study period. For the Reference, concentrations varied from 255 µmol l^{-1} (May) and 285 µmol l^{-1} (March) with an increase (up to 340 µmol l^{-1}) at 0.8 cm above the sediment. In the Rivière d'Auray, concentrations in the bottom waters under Oysters ranged from 165 µmol l^{-1} (August 1st) and 305 µmol l^{-1} (June). At the Reference, concentrations ranged from 200 µmol l^{-1} in August to 320 µmol l^{-1} in March. The concentration profiles of O_2 always showed a sharp negative concentration gradient presenting the sediment as a sink for dissolved oxygen whatever the season or the location. O_2 was always consumed within the first millimetres below the sediment-water interface. The penetration depths of dissolved oxygen profiles in the Aber Benoît ranged from 2 mm (August: Reference ; May: Oysters) to 3.8 mm (March: Oysters ; September: Reference). Nevertheless, a sporadic increase in O_2 concentrations was observed in the sediment in June and July in the Aber Benoît at the Reference. In the Rivière d'Auray, the penetration depths varied from 2.6 mm (September: Oysters ; June: Reference) to 4.7 mm (September: Reference).

The top sample of the pore water profiles was always impoverished in NO_3^- (as an example see figure 11) in relation to the bottom water, suggesting that the sediment is a sink for nitrate. By and large, NO_3^- vanished totally below 1 cm depth (Table 5 in Appendix).

No data were available for dissolved Fe and Mn in bottom waters. Mn^{2+} and Fe^{2+} pore water profiles (figure 7) indicated the sediment dissolution of Mn and Fe oxides. In the Aber Benoît, under Oysters, Fe^{2+} profiles highlighted an increase at depth where nitrate disappeared (up to 199 µmol l^{-1}) in March and May and at the end of September (up to 99 µmol l^{-1}). Then, concentrations decreased below 3-4 cm. At the other periods, concentrations were close to 10 µmol l^{-1} at all depths, both under Oysters and at the Reference. In the Rivière d'Auray, two maxima occurred in surficial sediments, the first one in March (Reference, up to 320 µmol l^{-1}) or May (Oysters, up to 221 µmol l^{-1}), the second in August (Oysters, up to 540 µmol l^{-1}) or in September more in depth (Reference, up to 232 µmol l^{-1}).

Mn^{2+} profiles (figure 7) generally displayed the same patterns as Fe^{2+} but with concentrations rarely exceeding 15 µmol l^{-1}.

Sulfide (H_2S, HS^-, S^{2-}) concentrations in sediments significantly differed between the two areas (figure 8). In the Aber Benoît, under Oysters, concentrations increased up to 4475 µmol l^{-1} at 7 cm depth in June and up to 2792 µmol l^{-1} at 4-7 cm depth in August (figure 8). At the Reference, concentrations were always lower than 70 µmol l^{-1} (figure 8). In the Rivière d'Auray, a different pattern occurred with lower concentrations (< 500 µmol l^{-1}) under Oysters compared to the Reference (up to 2415 µmol l^{-1} in May at 4-5 cm depth). Sulfide was never detected in the water column at either areas.

II.2.2. Phosphate and ammonium profiles

In both areas, phosphate concentrations in the bottom waters rarely exceeded 1 µmol l^{-1}. In the Aber Benoît, pore water phosphate concentrations were significantly higher under oysters compared to the Reference, with concentrations exceeding 70 µmol l^{-1} from 2 cm depth in May and June and from 4 to 7 cm depth in September (figure 8). At the Reference, concentrations rarely exceeded 10 µmol l^{-1}. On the contrary, in the Rivière d'Auray, both Oyster and Reference sites exhibited pore water concentrations seasonnaly higher than 70 µmol l^{-1} (figure 8). Surficial pore water concentrations were generally higher than in the Aber Benoît (20-30 µmol l^{-1} against 10-15 µmol l^{-1}). Ammonium profiles displayed the same behaviour as phosphate profiles but with about 20-30 and 8-12 times higher concentration levels, respectively in the Aber Benoît and the Rivière d'Auray (figure 8).

III.3. Calculated diffusive fluxes

Phosphate benthic fluxes (figure 9) calculated from pore water gradients using Equation (1) (§ II.6) ranged from 1 ± 0.1 µmol m^{-2} h^{-1} in September to 45 ± 11 µmol m^{-2} h^{-1} in June and from 1.8 ± 0.2 µmol m^{-2} h^{-1} in March to 19 ± 10 µmol m^{-2} h^{-1} in September, respectively in the Aber Benoît and in the Rivière d'Auray under Oysters. At the References, phosphate fluxes never exceeded 6 µmol m^{-2} h^{-1}.

A similar pattern was observed for ammonium under Oysters (figure 9), where fluxes varied from 68 ± 6 µmol m^{-2} h^{-1} (March) to 1014 ± 137 µmol m^{-2} h^{-1} (beginning of July) in the Aber Benoît and from 116 ± 16 µmol m^{-2} h^{-1} (March) to 317 ± 47 µmol m^{-2} h^{-1} (May) in the Rivière d'Auray. At the Reference, the highest ammonium fluxes appeared in May at both areas (39 ± 16 µmol m^{-2} h^{-1} in the Aber Benoît; 206 ± 47 µmol m^{-2} h^{-1} in the Rivière d'Auray).

Sulfide fluxes (figure 9) under Oysters, in the Aber Benoît, significantly increased in May, July and August (up to 510 µmol m^{-2} h^{-1}) whereas they were close to zero at the Reference. In the Rivière d'Auray, fluxes were generally higher under Oysters (up to 50 µmol m^{-2} h^{-1}), except in May and September (148 and 96 µmol m^{-2} h^{-1} at the Reference).

V. Discussion

The present study aimed to compare the impact of oyster farming on sediment properties and the phosphorus cycle in two contrasted estuaries. Our findings showed clear evidence of the seasonal impact of oyster cultures on sediment characteristics, mineralization processes and the phosphorus cycle in the Aber Benoît. In contrast, in the Rivière d'Auray, the occurence of macroalgae clearly masked this impact.

V.1 Impact of oyster culture on grain size and organic matter parameters

***A**quaculture activities are known to lead to an increase in fine particles in sediments, as in oyster cultures, where 95 % of particles of oyster feces and pseudofeces are less than 5 µm (Sornin, 1984). These biodepositions may increase sedimentation by a factor of 2-4, depending on the area (Nugues et al., 1996 ; Forrest and Creese, 2006). Grain Size distributions in the present study highlighted a different pattern in the two studied estuarine systems, i.e, a higher proportion of fine fractions under Oysters compared to the Reference, in the Aber Benoît, but not in the Rivière d'Auray (table 4). A decrease in water circulation due to rearing structures has usually been reported to explain the enhanced sedimentation beneath cultures (Kervella et al., 2010). In Aber Benoît, this phenomenon, associated with a relatively high density of oysters (39 tonnes per hectar) may have increased the sedimentation of fine particles beneath Oysters in spite of the high current velocities generally occurring in this estuary (around 0.8-1.3 m s^{-1}). At the Reference, located closer to the channel than the oyster structures, the stronger currents (Dyers, 1989) generated by high tides may have dispersed the fine particles over a large area.

In the Rivière d'Auray, lower current velocities (around 0-0.4 m s^{-1}) should have promoted silting under rearing structures and limited their dilution over the entire area. Our grain size data do not confirm this hypothesis. This could be explained by the 15 times lower density of oysters in the Rivière d'Auray (2-3 tonnes per hectar) than in the Aber Benoît. Moreover, low hydrodynamic conditions, favourable to water stagnation, making them more sensitive to anthropological inputs, could well explain the presence of green macroalgae, stranding regularly (Piriou et al., 1995), both under Oysters and at the Reference. These macroalgae, while increasing both organic matter and fine particles in sediments (Argese et al., 1992) could mask the biodeposition phenomenon under the rearing structures. Thus, macroalgae, and to a lesser extent, the transport of biodeposits from Oyster to Reference, may also explain the absence of significant differences ($p < 0.01$) in Orga-C, Chl a, Phaeopigments and Orga-P concentrations between the Oyster and Reference sites (figures 3 and 5).

In contrast, in the Aber Benoît, macroalgae deposits remained fixed to the rearing structures. As a matter of fact, the distribution of organic matter indicators in the Aber Benoît (Orga-C, Total N (not shown), Chl a and Phaeopigment) indicated a significant organic enrichment beneath Oyster compared to the Reference (figure 3), especially in May and June ($n = 12$; $p < 0.01$). The Chl a content of sediment beneath oysters in the Aber Benoît was probably enhanced by phytoplankton contained in the faeces and pseudofaeces of oysters, where a part of the Chl a has not been degraded (Barranget et al., 1994). Likewise, the increase in May and June of phaeopigments in sediment (figure 3) under Oysters could be due to bivalve metabolism as phaeopigments were shown to be linked to the feeding activity of molluscs (Barranget et al., 1997).

V.2. Mineralization of buried organic matter : consequences for nutrient release

Our data show common mineralization processes at all sites (1) but also a different fate of the buried organic matter between the two estuaries (2) and between reference and oyster sites (3). The intensity of mineralization is not always linked to organic matter levels in sediments as reported in other coastal shellfish areas (Mesnage et al., 2007).

(1) At both sites, mineralization of the buried organic matter followed the general sequence of early diagenetic reactions : oxygen was reduced in the surficial sediment (penetration depth lower than 5 mm). Nevertheless, net O_2 consumption rates (from about 2-3 µmol cm^{-3} d^{-1} in September to 7-10 µmol cm^{-3} d^{-1} in May ; Andrieux-Loyer et al., in prep.) do not reveal significant differences in mineralization between Oyster cultures and References, both in the Aber Benoît and in the Rivière d'Auray. O_2 consumption was followed by the reduction in nitrate, manganese oxides, iron oxides and sulfate. This induced seasonal accumulation of NH_4^+, HPO_4^{2-}, Mn^{2+}, Fe^{2+} and H_2S in the sediment, especially in the Aber Benoît under Oysters (figures 7 and 8). In the Rivière d'Auray, these parameters also highlighted the typical behaviour of the Reference as described above, ie, higher concentrations at the Reference. The increase in C/N (up to 9.6) and C/P (up to 315) from June to September and with depth (figure 4), high particulate Orga-C to Chl a ratios (>200 ; Table 4), and Chl a to (Chl a + pheophytin) ratio ~ 0.2-0.4 (data not shown) confirmed mineralization processes.

(2) However, COP/Chl a ratio- often used as an indicator of organic matter properties (Richard et al., 1997) -also pointed out a significantly different pattern beneath Oyters between the two estuaries. The significantly higher COP/Chl a ratios in the Rivière d'Auray compared to those in the Aber Benoît, suggested a more detrital organic pool (table 4). This could explain why, in the Rivière d'Auray, under Oysters, despite

concentrations of organic Carbon 1.5-2 times higher in surficial sediments (0-3 cm) than in the Aber Benoît (table 4 ; figure 3), the concentrations of mineralization products (ammonium, sulfide and to a lesser extent, phosphate ; figure 8) as well as their fluxes (figure 9) were relatively similar to or significantly lower (especially in June and July) than those reported in the Aber Benoît. We hypothesize that in the Rivière d'Auray there was a weaker degradation bacterial activity due to the nature of the organic matter (fewer biodeposits) but also to that of the bacterial community. Vibrio bacteria- particularly organotrophic- were more abundant in the Aber Benoît than in the Rivière d'Auray (Azanddegbe, 2010). The coarser nature of the sediments in the Aber Benoît compared to the Rivière d'Auray could also explain the different fate of the freshly deposited organic matter beneath Oysters. The rapid degradation of organic matter was shown to occur in coarse, permeable sediments (Bühring et al., 2006). In contrast, in fine-grained deposited sediments, remineralization could be delayed until late summer (Boon and Duineveld, 1998).

Nevertheless, at the Reference sites, a more conventional pattern occurred with the intensity of mineralization linked to organic matter levels in sediments. This was probably due to less difference in the nature of organic matter, as shown by COP/Chl a ratios in surficial sediments (table 4). In addition, surficial Orga-C concentrations at the References were significantly higher in the Rivière d'Auray compared to the Aber Benoît (up to 4.8 times higher, in August), which could mask different mineralization processes (table 4).

(3) A different fate of the buried organic matter was also observed between Oyster and Reference sites, especially in the Aber Benoît. Despite relatively low enrichment in Orga-C in the superficial sediments beneath Oyster compared to the Reference (a maximal factor around 1.5 in May 2008), fluxes of ammonia, phosphate and sulfide could be respectively up to around 70, 110 and 75 higher at the Oyster than at the Reference sites (figure 9). This suggests an efficient and rapid degradation of organic matter underneath oysters. This could not be explained by temperatures in the overlying and pore waters, similar for Oyster and Reference (figure 2) but rather by the nature of biodeposits shown to be rapidly decomposed compared to other organic material in coastal sediments (decay rates of phytoplankton and macroalgae 1.6 to 22 times lower than those of biodeposits; Giles and Pilditch, 2006).

V.3. Consequences for the phosphorus cycle

The cycle of phosphorus in sediment is strongly linked to the cycle of deposition/mineralization of organic matter. Our results show that the increase in labile organic matter, i.e biodeposits, beneath oysters significantly modifies the phosphorus cycle through the interactions of Fe, S and P.

In shallow marine environments, organic matter mineralization coupled to iron oxide reduction (state 1) and/or sulphate reduction (state 2) becomes the prominent process (Ekholm and Lehtoranta, 2012). In the present study, low dissolved iron concentrations (< 50 µmol l^{-1}) and sulfide concentrations higher than 3400 µmol l^{-1} beneath oysters in June and July in the Aber Benoît (figure 11) highlighted a shift from a system governed by iron oxide reduction (Reference) to a system where sulphate reduction dominates (beneath oysters). According to Lehtoranta et al., (2009), a major factor causing this shift from state 1 to state 2 is an increase in the input of labile organic matter to the sediment. This is in agrement with the increase in labile organic matter beaneath oysters in the Aber Benoît (see § V.2).

The presence of free sulfide was shown to enhance the release of dissolved phosphate in slurry experiments (Heijs et al., 2000), whereas the addition of iron salts could temporarily prevent phosphate exchange to the overlying water (Smolder et al., 2001). In the Aber Benoît, beneath oysters, the highest sulfide concentrations generally corresponded to the highest phosphate concentrations and to the lowest dissolved iron (figures 7 and 8). The decrease in dissolved iron could be explained by the formation of iron-sulfide compounds (FeS, FeS_2), which reduces adsorption sites for phosphate. Fe scavenging by hydrogen sulphide, -already reported in coastal systems (Boesen and Postma, 1988 ; Sundby et al., 1981)- has been shown to limit the upward transport of ferrous iron and subsequent re-precipitation of ferric iron at the oxic-anoxic boundary (Hupfer and Lewandowski, 2008). Phosphate is then released into the overlying water, wheras precipitated Fe is buried in the sediment. This decoupling of the Fe and P cycles -which occurs when sulphate reduction is the predominant process- decreases the availability of oxic surficial sediment to retain P. In the Aber Benoît beneath oysters, the significant correlations between sulfide and phosphate in the interstitial waters (r^2= 0.82 ; n = 16) and the absence of correlation between dissolved iron and phosphate concentrations ($r^2 < 0.01$), especially in June and July, as well as the significant increase in phosphate fluxes at the sediment-water interface at this period, reinforced the idea of the decoupling of Fe and P cycles. In addition, the decrease in adsorption sites for phosphate as sulfide availability increased was in agreement with the general trend of Fe-P concentrations decreasing with depth and from May to July in the Aber Benoît beneath oysters (figure 5).

The seasonal variations in pore water phosphate, sulfide and Fe^{2+} concentrations affected the pore water Fe:P (Fe^{2+}/ HPO_4^{2-}) and N:P ratios (NH_4^+/HPO_4^{2-}) and controlled the phosphate flux at the sediment-water interface. In coastal anoxic sediments such as those of the Aber Benoît and Rivière d'Auray, O_2 and also

NO_3^- are consumed in the first mm layers (see § V.2). Consequently, dissolved N/P ratios in pore water can be represented by NH_4^+/HPO_4^{2-} ratios.

The ratio between dissolved ammonium and phosphate (NH_4^+/HPO_4^{2-}) can supply information about the processes of phosphate release and uptake in the sedimentary cores (Ruttenberg and Berner, 1993 ; Schuffert et al., 1994). A constant ratio indicates a stoichiometric nutrient regeneration in which organic matter mineralization prevails. Variable ratios suggest that reactions of P removal or addition occur.

A decrease in molar ratio of dissolved Fe/P can also indicate high liberation of phosphate in the pore waters whithout corresponding high dissolved Fe^{2+} release from sediment to pore water (Rozan et al., 2002 ; Lehtoranta and Heiskanen, 2003).

At both studied sites, the lowest dissolved Fe/P ratios (figure 10) corresponded to the highest concentrations in sulfide as Fe^{2+} decreased through FeS formation (Sundby et al., 1992 ; Anschutz et al., 1998) and HPO_4^{2-} increased due to desorption (figure 8). Moreover, according to Stumm (1992), when Fe-oxide-PO_4 complexes are destroyed, PO_4 is solubilized while Fe^{2+} remains attached to the solid for some time. This could also partly explain the decrease in dissolved Fe/P ratios in pore waters exhibiting temporary anoxia, as those of in this study. At the same time, pore water N/P decreased (figure 10).

However, some other processes such as Auth-Ca-P formation could counterbalance the decrease in dissolved Fe/P and N/P ratios in scavenging dissolved phosphate (Ruttenberg, 1992 ; Raimonet et al., 2013). The enhanced liberation of pore water HPO_4^{2-} arising from Orga-P mineralization or from Fe-P dissolution should promote Auth-Ca-P precipitation (Slomp et al., 1996°; Raimonet et al., 2013). In the Aber Benoît, Auth-Ca-P precipitation and Fe-P precipitation in superficial sediments in May (beneath oysters) and in June and at the end of July in deeper layers (Reference), could partly explain the sharp rise in the ratio between dissolved ammonium and phosphate (NH_4^+/HPO_4^{2-}) and dissolved iron and phosphate (Fe^{2+}/HPO_4^{2-}) during these periods (respectively up to 70 and to 27). High N/P ratios indicated that mineralization alone cannot explain nutrient profiles and that HPO_4^{2-} removal and/or NH_4^+ formation must have taken place (Ruttenberg and Berner, 1993).

The formation of NH_4^+ by dissimilatory NO_3^- reduction (DNRA) in anoxic conditions already observed in anoxic coastal sediments could also increase NH_4^+/HPO_4^{2-} ratios (Gardner et al., 2002).

In contrast, in the Rivière d'Auray, the NH_4^+/HPO_4^{2-} ratios, close to or lower than 16, indicated that mineralization processes and Fe-P dissolution prevailed. This was in accordance with the low (< 3 µmol g^{-1}) and almost Auth-Ca-P constant concentrations over time (figure 5) and indicated that in this area, Auth-Ca-P probably did not contribute to the enrichment of the water column.

In the two areas, Auth-Ca-P -unlike Fe-P and Orga-P- was not significantly influenced by oyster cultures. However, in the Aber Benoît, the significant seasonal variations in Auth-Ca-P (Figure 5) indicated that this form of phosphorus- in the same way as Fe-P and Orga-P- could temporally behave as a sink for phosphate, then acting as a "time bomb" that could induce a modification in the trophic resource. In fact, if Auth-Ca-P has been generally considered as a sink for P (Ruttenberg and Berner, 1993 ; Andrieux-Loyer et al., 2008), it has also been shown that it could be redissolved (Spagnioli and Bergamini, 1997).

The precipitation and dissolution of Auth-Ca-P in sediments is controlled by pH and phosphate concentrations. Auth-Ca-P is precipitated at high pH and high HPO_4^{2-} activity (Stumm and Morgan, 1970). In this study, favorable conditions of Auth-Ca-P precipitation could occur after the sedimentation of labile organic matter beneath oysters (increase in phosphate concentrations due to mineralization processes), whereas the decrease in pH following mineralization processes could promote Auth-Ca-P re-dissolution. pH lower than 7-7.5 –already observed in coastal sediments- were shown to cause dissolution of weakly crystalline apatite (Stumm and Morgan, 1970 ; Stumm, 1992 ; Golterman, 1998).

Due to the complexity of processes governing phosphate fluxes at the sediment-water interface, some authors have suggested using dissolved Fe/P (Fe^{2+}/HPO_4^{2-}) ratios as an indicator of phosphate release in lake or marine sediments (Geurts et al., 2008 ; Jensen et al., 1992 ; Lehtoranta and Heiskanen, 2003).

The capacity of particles to retain or to liberate P was shown to depend on the stoichiometric ratio between dissolved iron and phosphate in surficial sediments. As freshly precipitated ferric oxides and phosphorus appear to form an aggregate structure with 2 moles of iron per each mole of phosphorus (Sugawara et al., 1957 ; Golterman, 1995), some authors have shown that the molar ratio of dissolved ferrous iron to dissolved phosphorus must be at least 2 in the pore water to ensure that newly formed ferric oxides can bind the released phosphate (Gunnars et al.,1997). Thus, ratios lower than 2 would mean that there is no enough iron to capture all the pore water phosphate in the superficial oxic layer, which would result in an increased benthic efflux of phosphate.

These ratios were generally lower in anaerobic marine systems than in freshwater systems due to high sulphate concentrations which can serve as a souce for sulphate reduction in conditions of a good supply of labile organic matter (Gunnars and Blomqvist, 1997 ; Zak et al., 2006).

In the Aber Benoît, maximal phosphate fluxes in June and July beneath oysters, corresponded to dissolved Fe/P molar ratios in surficial sediments significantly lower than the theoretical value of 2 mol:mol, corresponding to the complexation of Fe(OOH) with phosphate (figure 12). This indicated that in the Aber Benoît beneath oysters during the summer period, the available iron was in too short supply to bind all upward diffusing phosphate at the sediment water-interface. This induced a higher liberation of phosphate towards the water column (figures 9 and 12). At the other periods and at the Reference, the pore water ratios higher than 2 mol:mol indicated that there was enough dissolved Fe^{2+} to form a superficial Fe^{3+} oxide layer which could retain the up-ward diffusing phosphate. In the Rivière d'Auray, the shift from state 1 to state 2 (figure 12) was less marked, probably due to the nature of the organic matter, i.e, mostly macroalgae, less labile than biodeposits (see § V.2). Nevertheless, at the Reference, the highest phosphate flux in May corresponded to the lowest Fe/P ratio (< 2 mol:mol), and to the highest sulfide and phosphate concentrations (figure 8).

CONCLUSION

Our results highlight the influence of oyster cultures on biogeochemical processes in the sediments of the Aber Benoît, especially concerning the phosphorus cycle. In contrast, in the Rivière d'Auray, the occurrence of macroalgae at both Reference and Oyster sites masked the impact of oysters.

The intensity of organic matter mineralization beneath oysters, as highlighted by diffusive fluxes of mineralization products, was lower in the Rivière d'Auray than in the Aber Benoît despite organic matter levels being 1.5-2 times higher. This could be explained by the less labile nature of organic matter in the Rivière d'Auray (fewer biodeposits) than in the Aber Benoît, as shown by COP/ Chl a ratios.

In the Aber Benoît, the increase in labile organic matter (ie biodeposit) beneath oysters seasonally increased outfluxes of ammonium, sulfide and phosphate due to mineralization processes. The enhanced phosphate availability was also explained by the less effective scavenging of phosphate by iron hydroxides, as sulfide formed iron sulfide compounds. This release of phosphate appeared to increase significantly when dissolved Fe/P ratios dropped below a value of 2. This additional seasonally released P may significantly increase the biologically available pool of P in the water, thus modifying the trophic resource. Oyster cultures could consequently lead to long term modifications in the capacity of the sediment in scavenging/liberating phosphate.

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Table 1

Main characteristics of Aber Benoît and Rivière d'Auray

	Aber Benoît	**Rivière d'Auray**
Location	**North-west Brittany** **4°36'W and 48°36'N**	**Gulf of Morbihan** **South Britanny** **2°58'W and 47°36'N**
Catchment area	**140 km^2**	**800 km^2**
Anthropic influence	+	+++
Oyster culture **Annual production/area**	**1500t/38 ha**	**4500t/1635 ha**
Depth at zero tide	**14 m**	**20 m**
Mean tidal range	**6 m**	**5 m**
Sea-water current	**0.8-1.3 m s^{-1}**	**0-0.4 m s^{-1}**
Sediment	**Grey sandy mud**	**Black sandy mud**

Table 2

Sequential extraction method for phosphorus forms in sediments ; Adsorbed and iron-oxide bound P (Fe-P) and Authigenic calcium bound P (Auth-Ca-P) after Psenner, 1988 ; Ruttenberg, 1990 ; Slomp, 1996a and Organic phosphorus (Orga-P ; Aspila, 1992).

Step	Extractant and Protocol	Phase extracted
I) Adsorbed + iron-bound	0.1 mol l^{-1} Dithionite-Bicarbonate (DB) , 8 h, 20 °C	Exchangeable or loosely sorbed P + easily reducible Fe-bound P
II) Authigenic (Auth-Ca-P)	a) 1 mol l^{-1} Na-acetate buffer (pH = 4, 6 h, 20 °C) b) washing with 1 mol l^{-1} $MgCl_2$, (pH = 8, 0.5 h, 20 °C)	Carbonate fluoroapatite (CFA) + biogenic hydroxyapatite + $CaCO_3$-bound P
III) Organic*	a) 1 mol l-1 HCl treatment overnight (inorganic P) b) Ash at 550 °C, then 1 mol l^{-1} HCl treatment overnight (total P)	Organic P (Total P –inorganic P)

** Note that Orga-P extraction (step III) was performed non-sequentially on a separated sub-sample.*

Table 3

Ammonium, phosphate and sulfide concentrations in Overlying Water (OW) and pore water used in diffusive flux calculations both in Aber Benoît and Rivière d'Auray.

Site	Date	Depth[1] cm	Depth[2] cm	Oyster Ammonium µM C1	Oyster Ammonium µM C2	Oyster Ammonium µM C3	Reference Ammonium µM C1	Reference Ammonium µM C2	Reference Ammonium µM C3	Oyster Phosphate µM C1	Oyster Phosphate µM C2	Oyster Phosphate µM C3	Reference Phosphate µM C1	Reference Phosphate µM C2	Reference Phosphate µM C3	Oyster Sulfide µM C1	Reference Sulfide µM C1
Aber Benoît																	
	12/03	OW	4	2.5	2.9	2.32	2.38	2.64	2.32	0.7	0.77	0.7	0.76	0.77	0.75	250	7
		0-0.5	6.5	79	63	60	33	47	42	2.8	1.1	2.8	3.8	2	3.6	693	10
	6/05	OW	4	1.35	1.35	1.29	1.48	1.48	1.61	0.34	0.42	0.37	0.42	0.43	0.43	374	56
		0-0.5	6.5	174	195	141	73	56	29	10.2	11.5	5.5	10.1	3.8	3	3145	67
	02/06	OW	2.5	1.61	1.99	1.8	1.54	2.12	1.61	0.36	0.42	0.41	0.43	0.45	0.44	729	5
		0-0.5	4	741	807	757	41	65	45	62	168	174	5.3	6.6	6.5	3214	23
	3/07	OW	1.25	3.42	9.01	12.3	3.24	3.36	3.1	0.53	0.75	1.2	0.67	0.66	0.71	645	10
		0-0.5	1.75	496	1346	1438	33	17	20	21.3	115	129	3	1.89	1.98	1358	13
	31/07	OW	4	2.14	2.8	1.8	2.69	2.69	2.57	0.49	0.53	0.4	0.58	0.58	0.57	323	12
		0-0.5	6.5	178	175	148	13.4	18	16	2.79	2.9	2.4	1	1	1.3	887	13
	30/08	OW	2.5	1.71	1.16	1.45	1.4	1.22	7	0.38	0.35	0.7	0.37	0.4	0.34	1370	13
		0-0.5 cm	4	182	158	155	28.1	27	21	11	7.4	7	4.2	3.16	3.7	2792	20
	27/09	OW	4	3	3	28	1.48	1.6	1.4	0.44	0.5	0.3	0.44	0.4	0.4	607	13
		0-0.5	6.5	209	217	229	33	62	39	2.44	2.69	2.11	5.5	4.72	3.98	1487	18
Rivière d'Auray	**13/03**	OW	2.5	5.28	5.02	6.11	3.8	3.86	3.73	0.59	0.57	0.64	0.48	0.48	0.48	2	6
		0-0.5	4	125	80	121	55	31	57	5.3	4.2	5.5	4.3	3	2	227	12
	7/05	OW	2.5	3.02	3.41	2.64	5.34	6.37	3.02	0.22	0.26	0.23	0.54	0.58	0.27	12	1439
		0-0.5	4	193	210	151	145	110	86	14.4	56.7	9.9	12	3	10	88	2415
	06/06	OW	6	4.57	4.31	4.44	7.85	6.56	5.08	0.44	0.41	0.41	0.76	0.54	0.7	141	5
		0-0.5	8.5	222	219	202	102	129	120	29.3	27.5	29.6	10	5.3	3.1	205	108
	4/07	OW	1.75	3.98	8.44	2.14	2.39	2.26	1.65	0.69	1.11	0.48	0.57	0.54	0.47	13	8
		0-0.5	2.5	173	125	137	68	60	51	27.4	22.2	20.3	3.6	4	6	49	20
	1/08	OW	4	5.75	5.63	10.8	1.65	1.53	2.63	1.05	0.91	0.68	1.13	0.64	0.76	10	9
		0-0.5	6.5	117	153	105	94	82	68	4.4	6.6	4.6	9.1	7	8.5	25	10
	31/08	OW	4	5.05	5.36	7.12	9.97	4.68	2.83	0.73	0.78	0.91	1.24	0.78	0.58	293	15
		0-0.5	6.5	118	109	116	39	74	35	23.1	19.3	17.7	2.6	6	1.5	457	31
	29/09	OW	1.5	4.1	3.73	4.4	2.02	1.71	2.63	0.93	0.83	0.72	0.67	0.53	0.62	15	457
		0-0.5	2.5	161	161	88	4.3	2.4	6.7	65	24	30	2.9	4	4	34	1219

Units are in $\mu mol\ l^{-1}$.
Depth[1]: depth taken into account in ammonium and phosphate flux calculations
Depth[2]: depth taken into account in sulfide flux calculations
C1, C2, C3: Cores 1, 2 and 3.

Table 4

Surficial sediment (in the top 3 cm) characteristics at each study site over the study period.

Study site	**Aber Benoît**		**Rivière d'Auray**	
	Under Oysters	Reference	Under Oysters	Reference
n	31	31	33	33
Granulometry Silt + Clay (%)	**34** (3)	**25** (5)	**67** (4)	**70** (5)
Porosity (%)	**65** (5)	**60** (3)	**81** (2)	**82** (2)
C (µmol g-1)	**950** (333)	**764** (246)	**1426** (753)	**1728** (279)
N (µmol g-1)	**139** (40)	**109** (39)	**223** (53)	**270** (50)
Orga-P (µmol g-1)	**3.8** (1.4)	**3.0** (1.3)	**5.2** (1.6)	**6.2** (1.9)
C/N	**8** (0)	**7** (1)	**7** (0)	**7** (0)
C/P (COP/POP)	**250** (64)	**271** (95)	**326** (108)	**314** (118)
N/P	**39** (26)	**34** (16)	**49** (15)	**47** (16)
COP/Chl a	**694** (250)	**787** (330)	**1459** (785)	**1036** (540)

Mean (bold type) and standard deviation (in parentheses)
n= number of observations

Figure Captions

Figure 1. Study areas. A) Main situation ; B_1) The Aber Benoît ; B_2) The Rivière d'Auray.

Figure 2. Summary of overlying physical-chemical water properties (temperature, salinity, pH) in Aber Benoît (1a) and in Rivière d'Auray (1b) during the study period (2007-2008). (**O:** beneath Oyster ; R: Reference). *Salinity is expressed on the PSS78 scale.*

Figure 3. Organic Carbon (Orga-C) and Phaeopigments + Chlorophyll a (Chl a) seasonal distributions in sediments (2007-2008) in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites. The concentration units are in µmol g^{-1} for Orga-C and µg g^{-1} for Phaeopigments and Chl a.

Figure 4. Orga C/N, Orga C/P seasonal distributions in sediments (2007-2008) in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites.

Figure 5. Phosphorus forms (adsorbed and iron-oxide bound P (Fe-P), Organic P (Orga-P), Authigenic Calcium bound P (Auth-Ca-P) seasonal distributions in sediments (2007-2008) in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites. The concentrations units are in µmol g-1.

Figure 6. Oxygen microprofiles (µmol l^{-1}) acquired by microelectrodes in function of depth (mm) during the study period in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites.

Figure 7. Manganese (Mn^{2+}) and iron Fe^{2+})seasonal distributions in pore water sediments (2007-2008) in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites. The concentration units are in µmol l^{-1}.

Figure 8. Ammonium (NH_4^+), phosphate (HPO_4^{2-}) and sulfide (HS^-) seasonal distributions in pore water sediments (2007-2008) in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites. The concentration units are in µmol l^{-1}

Figure 9. Seasonal variations of mean diffusive fluxes (Phosphate, Ammonium, Sulfide) in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites. *Diffusive fluxes are determined from three cores for nutrients and from one core for sulfide and are expressed in µmol m^{-2} h^{-1}. Coefficients of variation ranged between 5 – 20 %. In order to facilitate comparisons between Aber Benoît and Rivière d'Auray, the same scale was used for each study area.*

Figure 10. Dissolved N/P and Fe/P ratios seasonal distributions in pore water sediments (2007-2008) in the Aber Benoît and in the Rivière d'Auray both under Oysters and at Reference sites.

Figure 11. Sulfide (HS-), phosphate (HPO_4^{2-}), dissolved iron (Fe^{2+}) and nitrate (NO_3^-) profiles over depth in June in the Aber Benoît at the Reference (1) and beneath Oysters (2). Concentrations are expressed in μmol l^{-1}.

Figure 12. Dissolved Fe:P ratios in surface layer of pore water and diffusive fluxes of phosphate (μmol m^{-2} h^{-1}). Vertical dotted line represents theorical molar dissolved Fe:P ratio (2 mol:mol). *For clarifying, sampling dates are only indicated for the most characteristics results.*

Figure 1 A et B

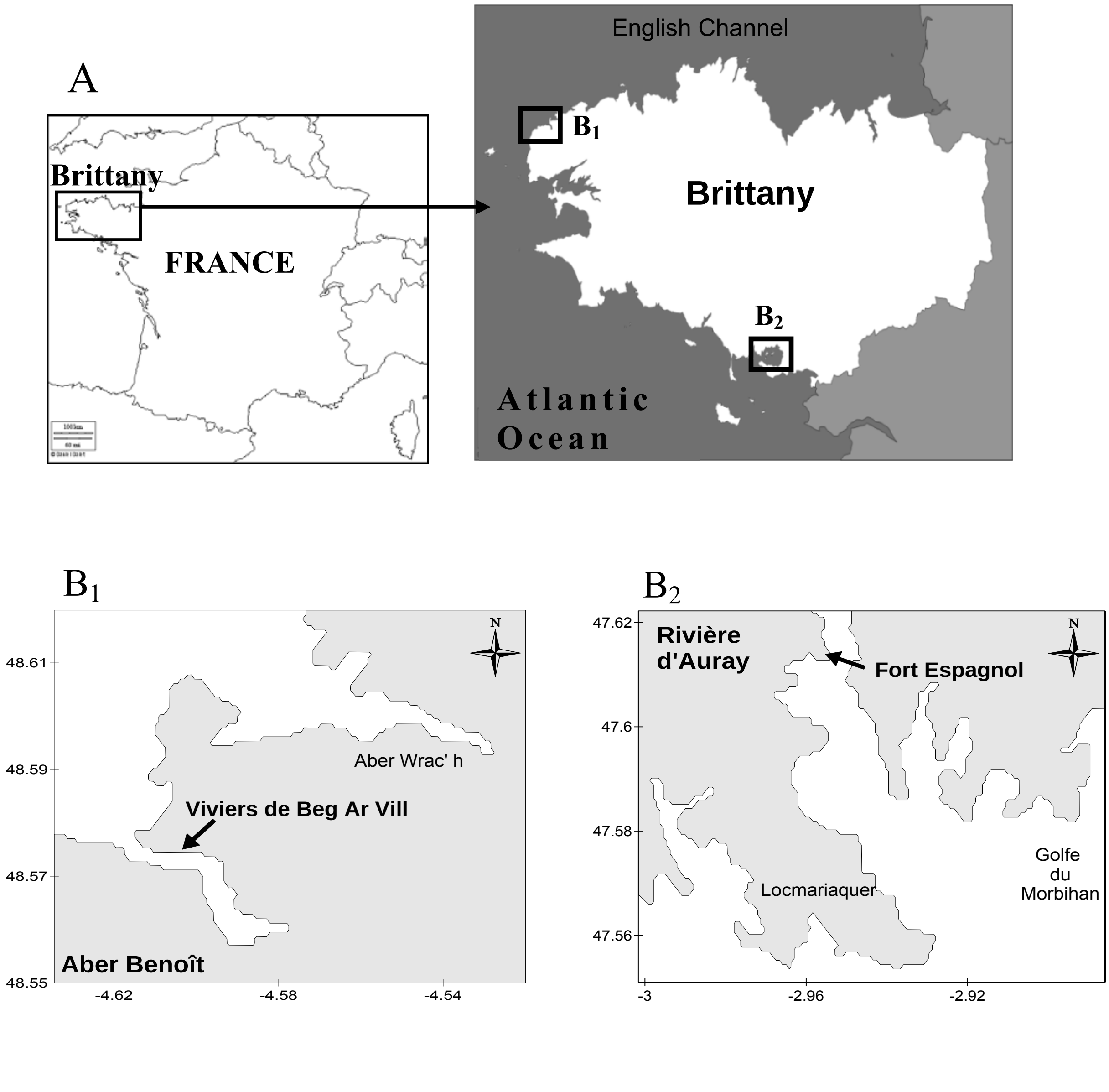


Figure 2 A et B

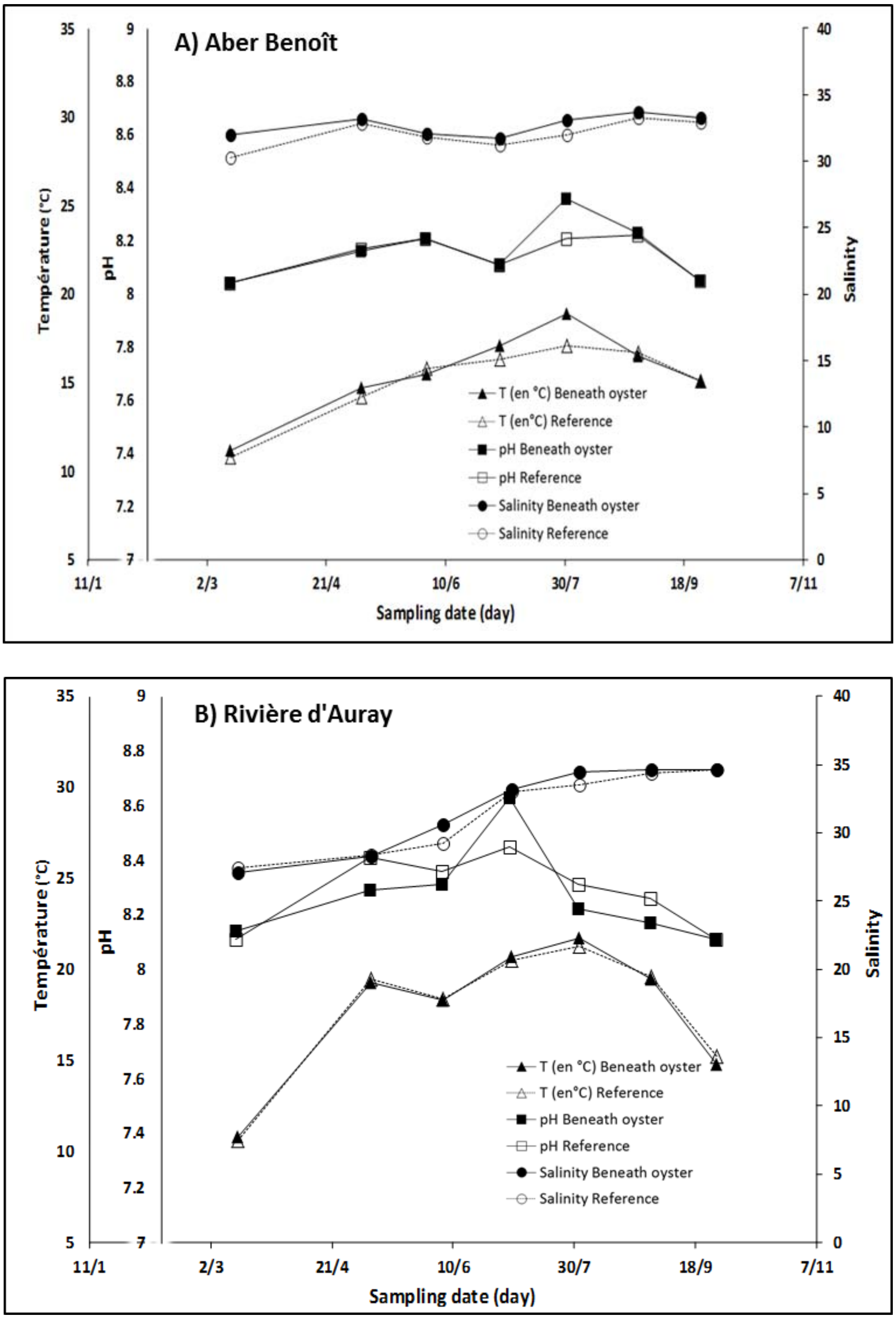


Figure 3

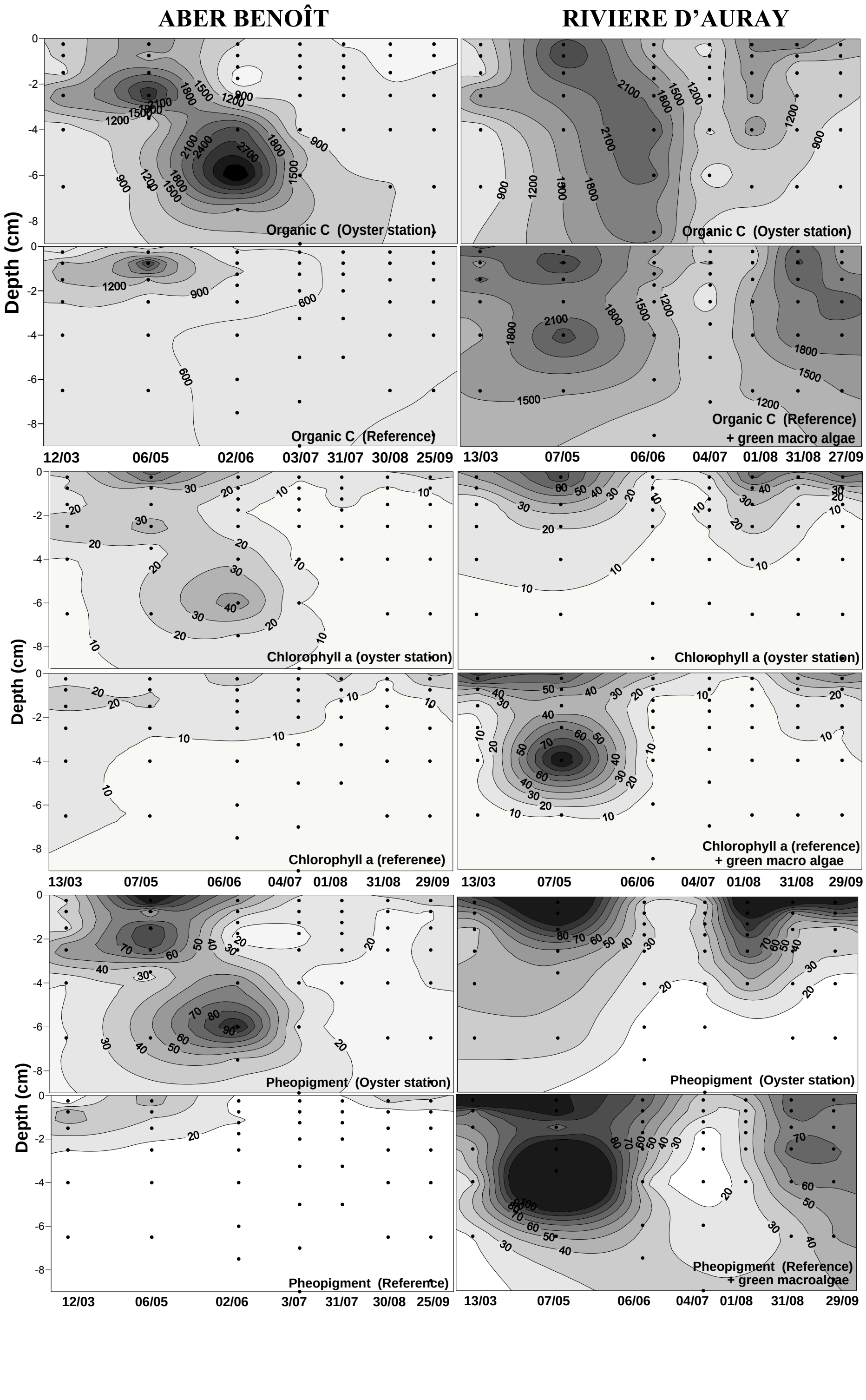

ABER BENOÎT
RIVIERE D'AURAY
Depth (cm)
Organic C (Oyster station)
Organic C (Reference)
Organic C (Reference)
+ green macro algae
12/03 06/05 02/06 03/07 31/07 30/08 25/09
13/03 07/05 06/06 04/07 01/08 31/08 27/09
Chlorophyll a (oyster station)
Chlorophyll a (reference)
Chlorophyll a (reference)
+ green macro algae
13/03 07/05 06/06 04/07 01/08 31/08 29/09
Pheopigment (Oyster station)
Pheopigment (Reference)
Pheopigment (Reference)
+ green macroalgae
12/03 06/05 02/06 3/07 31/07 30/08 25/09
13/03 07/05 06/06 04/07 01/08 31/08 29/09

Figure 4

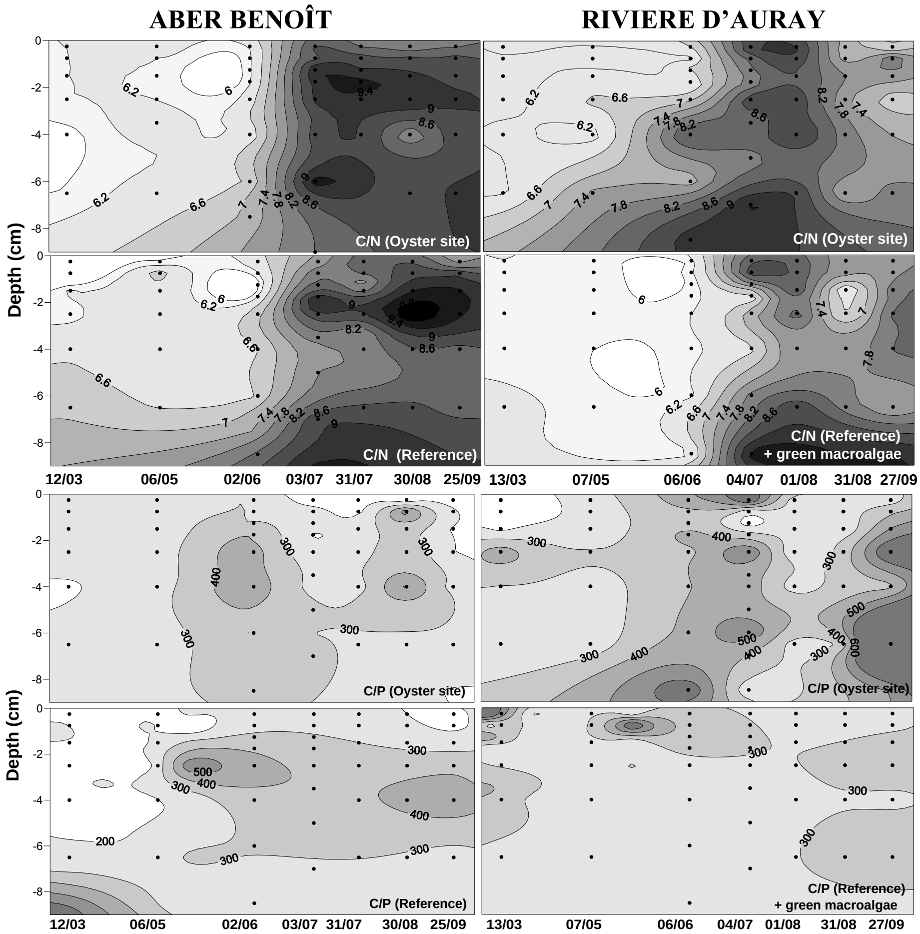

ABER BENOÎT
RIVIERE D'AURAY
C/N (Oyster site)
C/N (Reference)
C/N (Reference)
+ green macroalgae
C/P (Oyster site)
C/P (Reference)
C/P (Reference)
+ green macroalgae
Depth (cm)
12/03 06/05 02/06 03/07 31/07 30/08 25/09
13/03 07/05 06/06 04/07 01/08 31/08 27/09

Figure 5

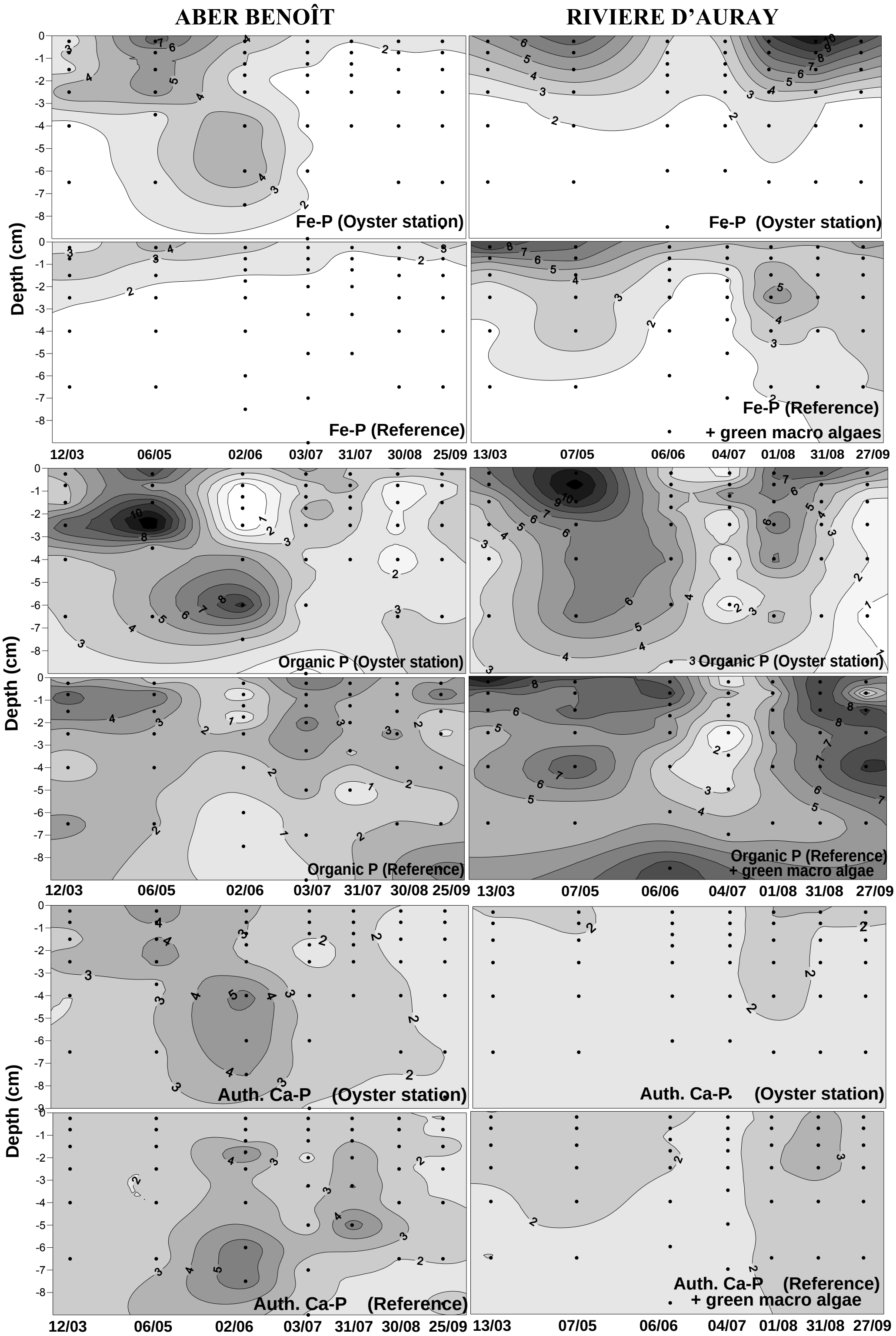
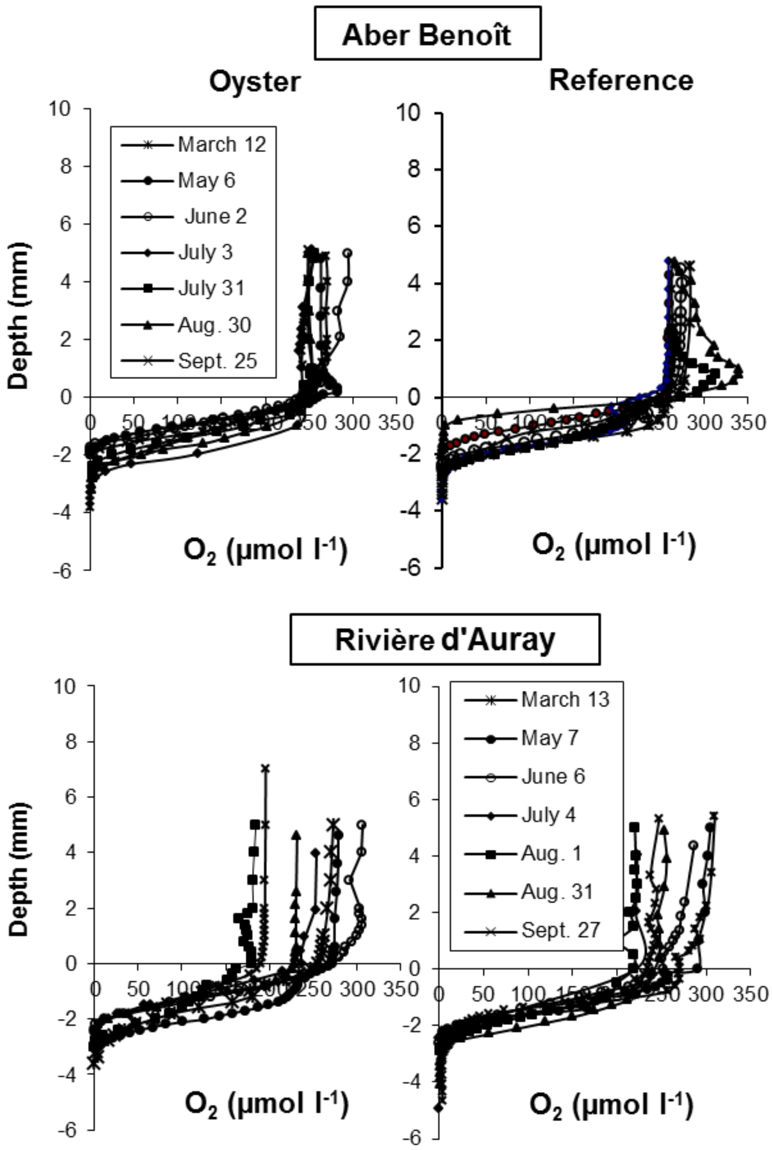
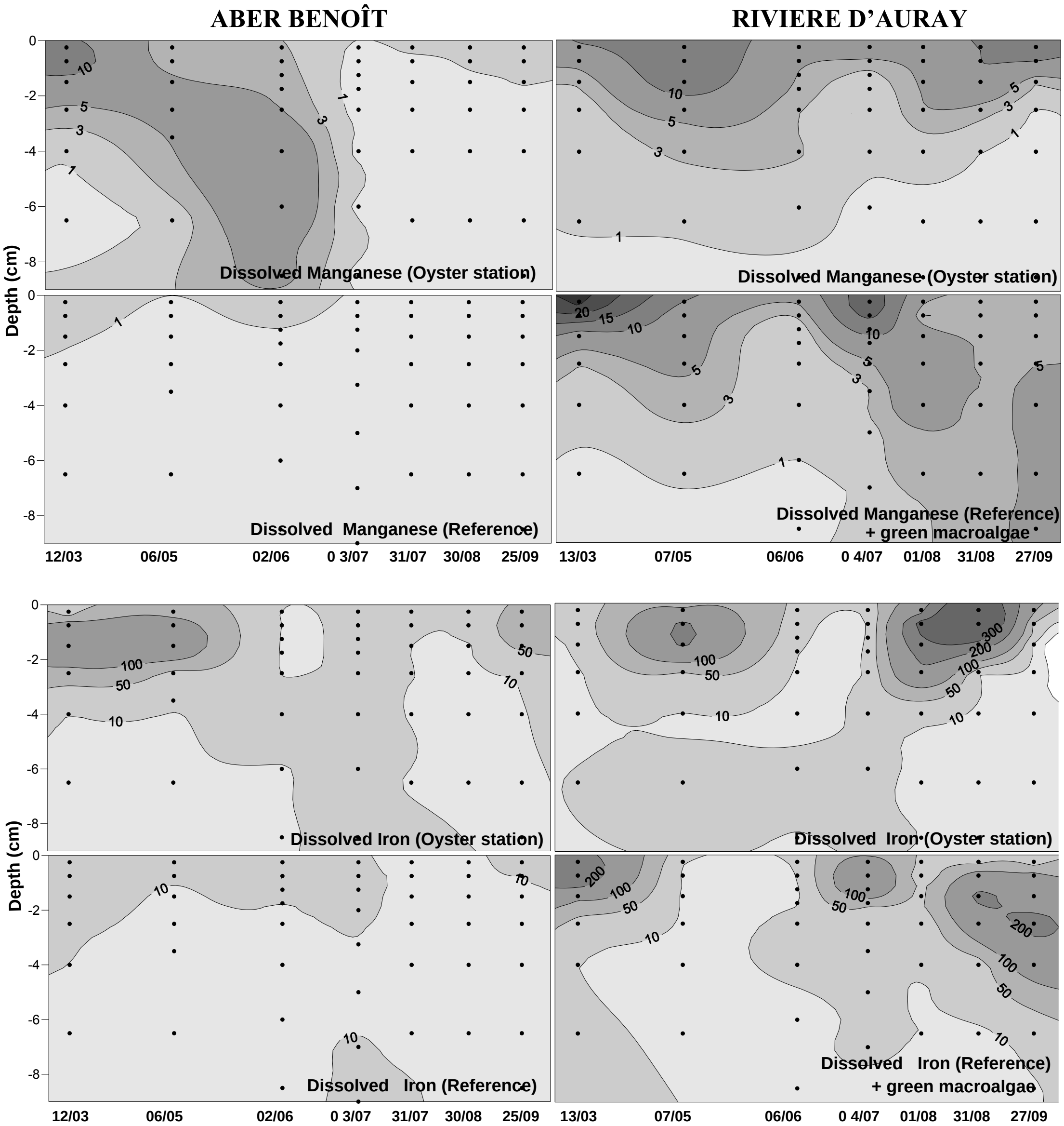

ABER BENOÎT
RIVIERE D'AURAY
Depth (cm)
Fe-P (Oyster station)
Fe-P (Oyster station)
Fe-P (Reference)
Fe-P (Reference)
+ green macro algaes
12/03 06/05 02/06 03/07 31/07 30/08 25/09
13/03 07/05 06/06 04/07 01/08 31/08 27/09
Organic P (Oyster station)
Organic P (Oyster station)
Organic P (Reference)
Organic P (Reference)
+ green macro algae
Auth. Ca-P (Oyster station)
Auth. Ca-P. (Oyster station)
Auth. Ca-P (Reference)
Auth. Ca-P (Reference)
+ green macro algae

Figure 6



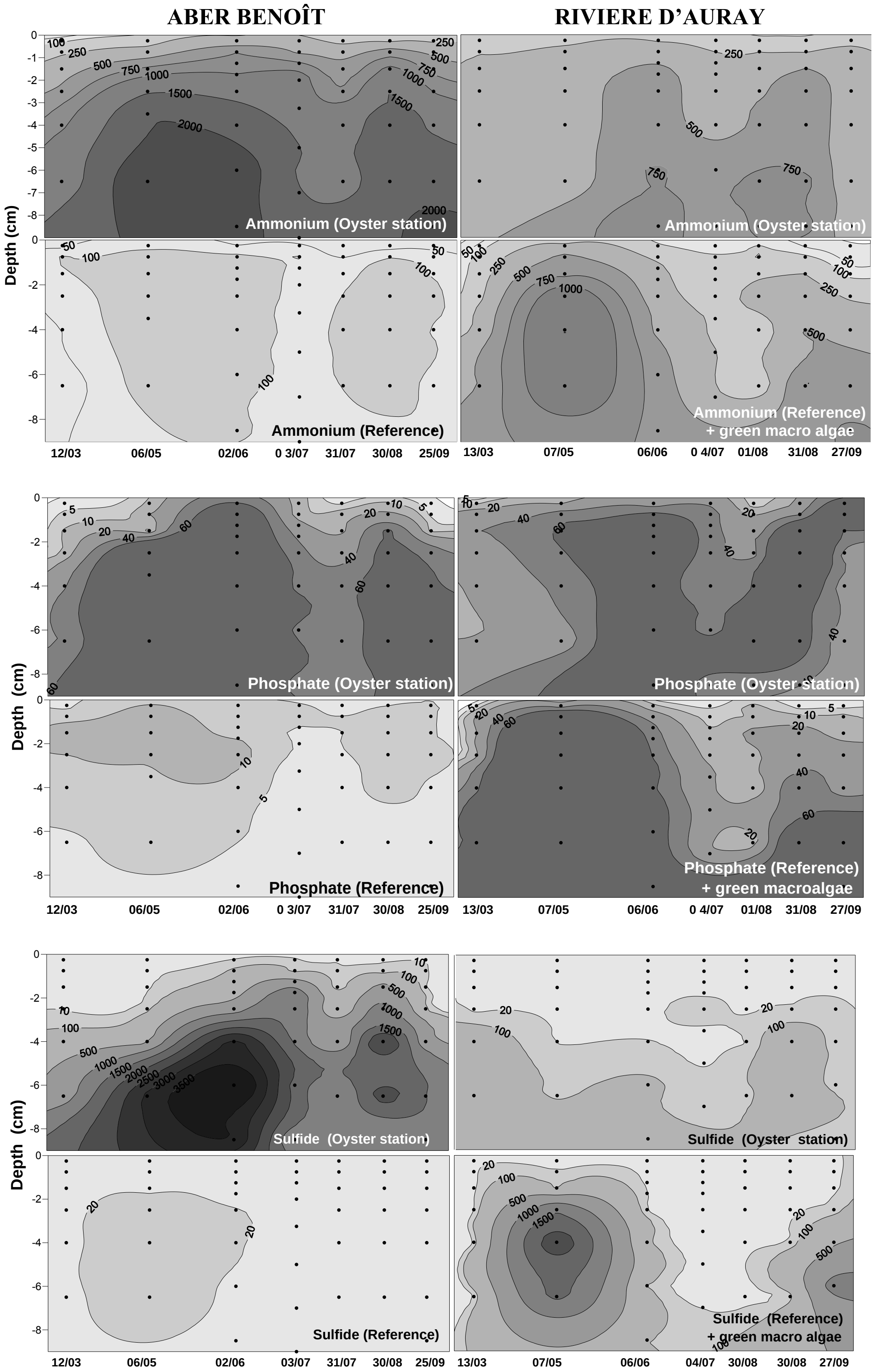
Aber Benoît
Oyster
Reference
Depth (mm)
March 12
May 6
June 2
July 3
July 31
Aug. 30
Sept. 25
O2 (µmol l-1)
Rivière d'Auray
March 13
May 7
June 6
July 4
Aug. 1
Aug. 31
Sept. 27

Figure 7



ABER BENOÎT
RIVIERE D'AURAY
Depth (cm)
Dissolved Manganese (Oyster station)
Dissolved Manganese (Reference)
Dissolved Manganese (Reference) + green macroalgae
Dissolved Iron (Oyster station)
Dissolved Iron (Reference)
Dissolved Iron (Reference) + green macroalgae
12/03
06/05
02/06
0 3/07
31/07
30/08
25/09
13/03
07/05
06/06
0 4/07
01/08
31/08
27/09

Figure 8



ABER BENOÎT
RIVIERE D'AURAY
Depth (cm)
Ammonium (Oyster station)
Ammonium (Oyster station)
Ammonium (Reference)
Ammonium (Reference)
+ green macro algae
12/03
06/05
02/06
0 3/07
31/07
30/08
25/09
13/03
07/05
06/06
0 4/07
01/08
31/08
27/09
Phosphate (Oyster station)
Phosphate (Oyster station)
Phosphate (Reference)
Phosphate (Reference)
+ green macroalgae
Sulfide (Oyster station)
Sulfide (Oyster station)
Sulfide (Reference)
Sulfide (Reference)
+ green macro algae

Figure 9

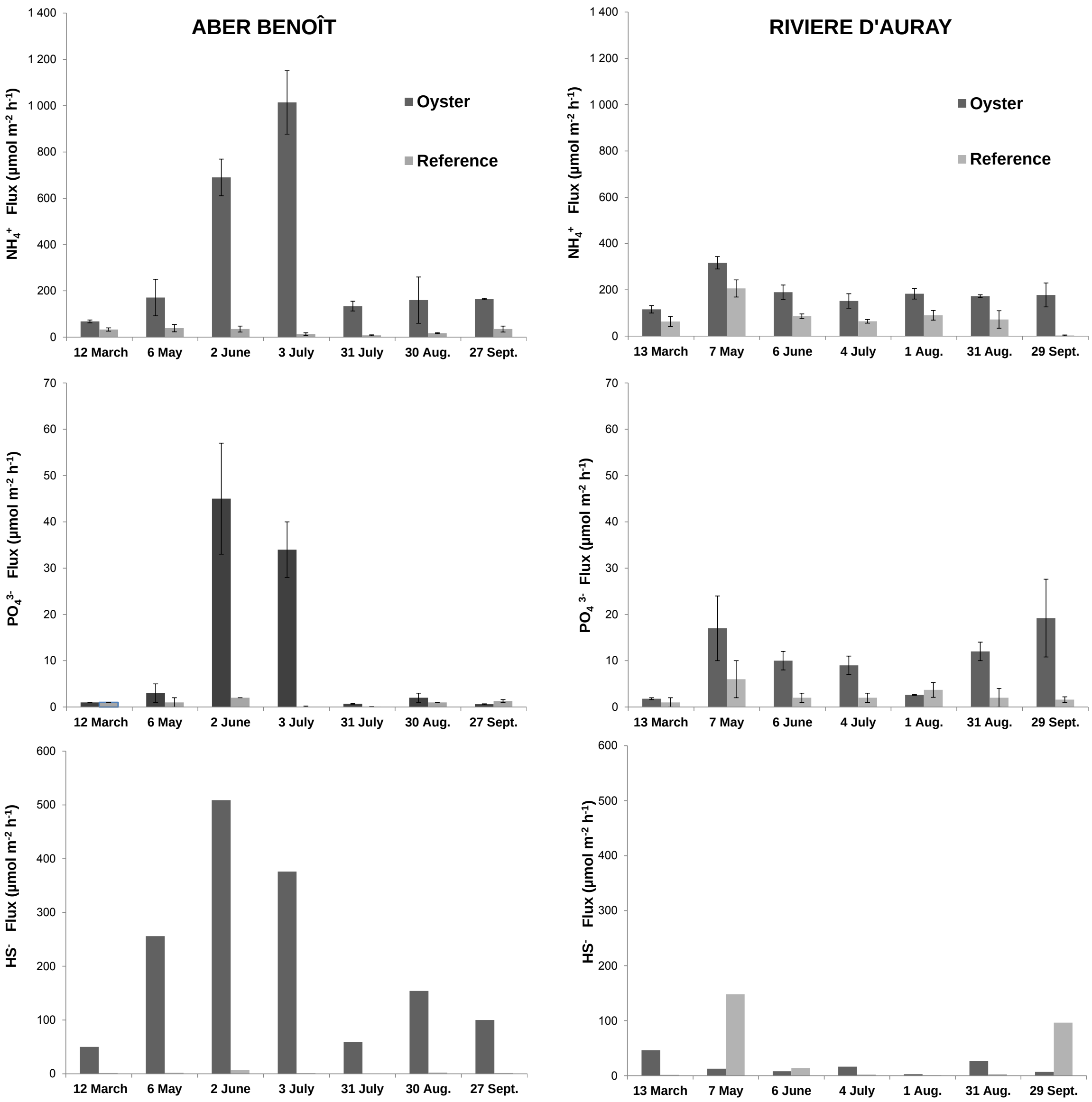

ABER BENOÎT
RIVIERE D'AURAY
Oyster
Reference
NH4+ Flux (µmol m-2 h-1)
PO4 3- Flux (µmol m-2 h-1)
HS- Flux (µmol m-2 h-1)
12 March
6 May
2 June
3 July
31 July
30 Aug.
27 Sept.
13 March
7 May
6 June
4 July
1 Aug.
31 Aug.
29 Sept.

Figure 10

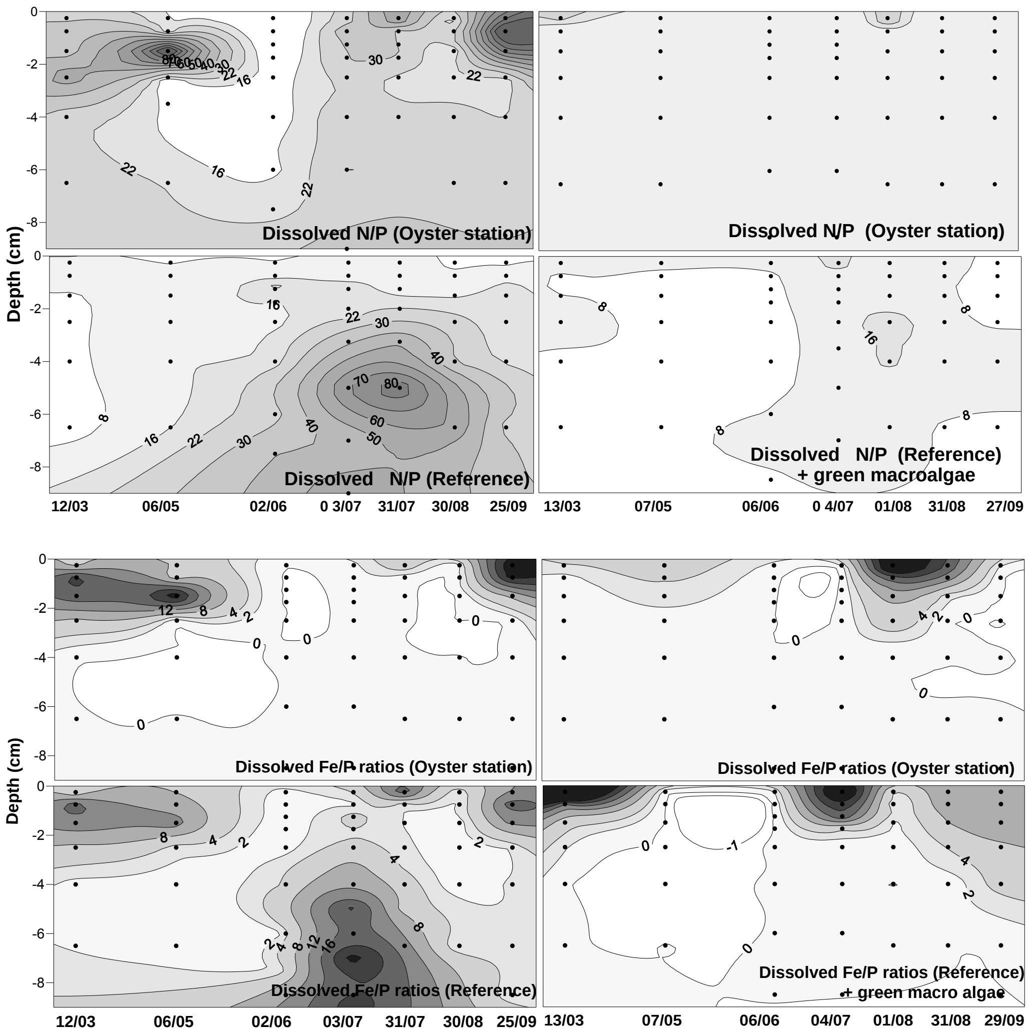
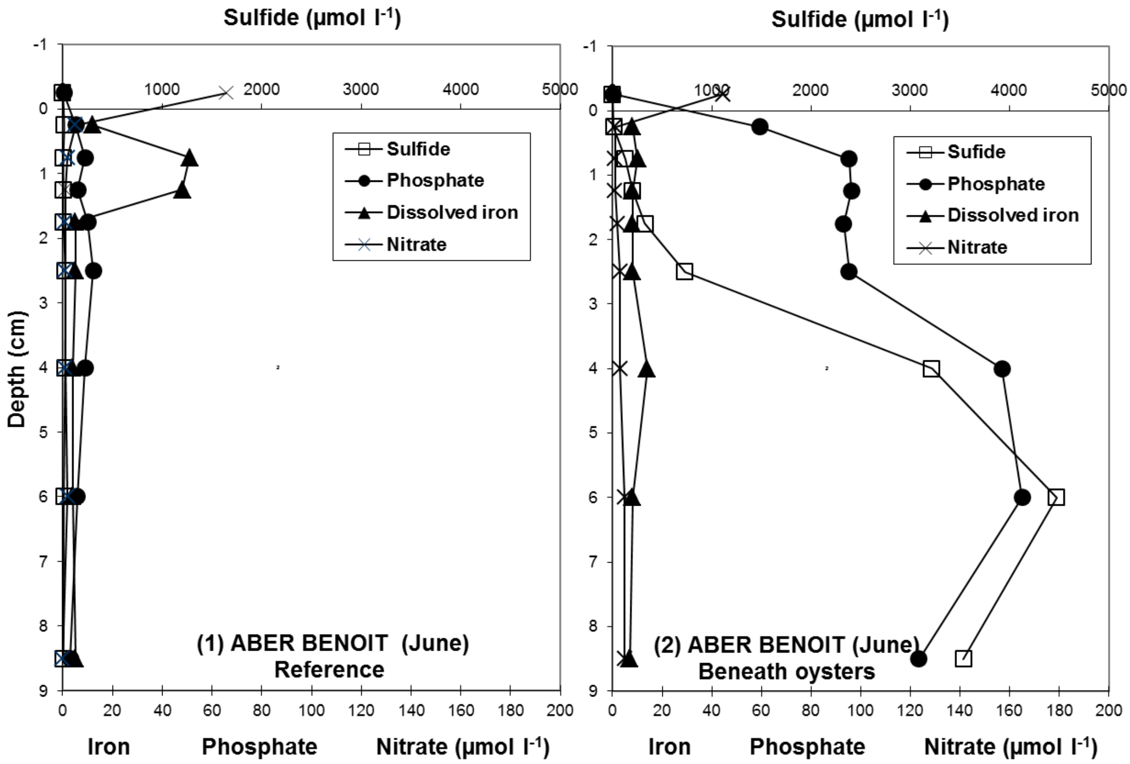
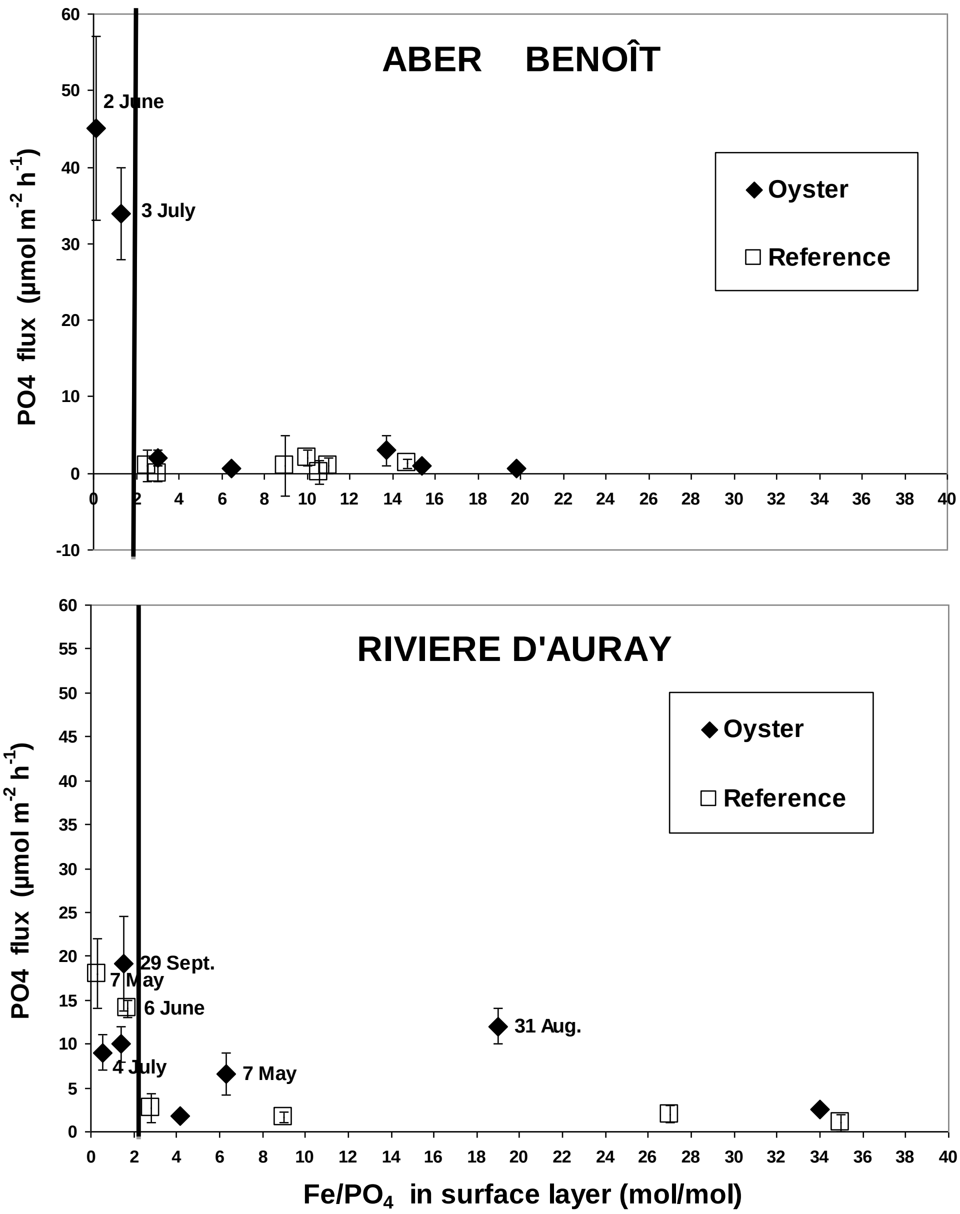

Dissolved N/P (Oyster station)
Dissolved N/P (Oyster station)
Dissolved N/P (Reference)
Dissolved N/P (Reference)
+ green macroalgae
Depth (cm)
12/03 06/05 02/06 0 3/07 31/07 30/08 25/09
13/03 07/05 06/06 0 4/07 01/08 31/08 27/09
Dissolved Fe/P ratios (Oyster station)
Dissolved Fe/P ratios (Oyster station)
Dissolved Fe/P ratios (Reference)
Dissolved Fe/P ratios (Reference)
+ green macro algae
Depth (cm)
12/03 06/05 02/06 03/07 31/07 30/08 25/09
13/03 07/05 06/06 04/07 01/08 31/08 29/09

Figure 11



Sulfide (µmol l-1)
Depth (cm)
Sulfide
Phosphate
Dissolved iron
Nitrate
(1) ABER BENOIT (June)
Reference
Iron
Phosphate
Nitrate (µmol l-1)
Sulfide (µmol l-1)
Sufide
Phosphate
Dissolved iron
Nitrate
(2) ABER BENOIT (June)
Beneath oysters
Iron
Phosphate
Nitrate (µmol l-1)

Figure 12



ABER BENOÎT
2 June
3 July
Oyster
Reference
PO4 flux (µmol m-2 h-1)
RIVIERE D'AURAY
29 Sept.
7 May
6 June
4 July
7 May
31 Aug.
Fe/PO4 in surface layer (mol/mol)

Appendix

See table 5

Seasonal distributions (2007-2008) of particulate parameters (Phosphorus forms (adsorbed and iron-oxide bound P (Fe-P), Organic P (Orga-P), Authigenic Calcium bound P (Auth-Ca-P), Organic Carbon (Orga-C), Total Nitrogen (Total N), Chlorophyll a (Chl a), Phaeopigments) and dissolved parameters (Nitrate (NO_3^-), Ammonium (NH_4^+), phosphate (HPO_4^{2-}) and sulfide (HS^-)) in sediments of the Aber Benoît and the Rivière d'Auray both under Oyster and at Reference sites. Phosphorus forms, Orga-C, Total N, are expressed in µmol g^{-1}. Chl a, phaeopigments are expressed in µg g^{-1} and dissolved parameters in µmol l^{-1}.

NH_4^1, PO_4^1 : Concentrations in core 1

NH_4^2, PO_4^2 : Mean concentrations for core 1, 2 and 3.

Table 5

ABER BENOÎT (OYSTER)																
Date	Depth	Fe-P	Auth-Ca-P	Orga-P	Orga-C	total N	Chlo a	Pheopigment	NO_3^-	NH_4^1	NH_4^2	PO_4^1	PO_4^2	HS^-	Fe^{2+}	Mn^{2+}
	cm			µmol g^{-1}				µg g^{-1}				µmol l^{-1}				
12/03	-0.25	2.3	3.6	4.4	963	184	19.0	27	2.0	79	*67(10)*	2.8	2.2(1.0)	7.1	25	11
	-0.75	3.3	3.2	3.9	1004	174	20.5	35	0.84	220	*212(22)*	6.2	5.4(1.7)	9.8	131	14
	-1.5	2.7	2.6	3.5	757	162	14.8	24	0.77	375	-	10.9	-	10.1	199	8
	-2.5	4.8	3.6	8.1	1846	312	29.6	60	0.91	547	-	9.8	-	7.7	70	4.4
	-4	1.5	2.0	3.4	656	119	8.5	20	2.93	926	-	37.2	-	250	10	1.1
	-6.5	1.4	2.1	3.1	664	110	7.0	19	2.93	1163	-	41.7	-	693	7	0.2
06/05	-0.25	7.7	4.3	9.1	1872	288	66.5	122	7.9	174	*170(27)*	10.2	9.1(3.2)	10.4	81	2.9
	-0.75	5.0	4.0	4.8	1282	207	22.7	45	1.80	332	*308(28)*	20.0	21.4(1.4)	1.8	126	3.9
	-1.5	5.2	4.0	8.9	2019	329	18.5	92	0.84	802	-	6.6	-	2.1	178	5.5
	-2.5	5.5	4.3	12.5	3115	542	37.0	83	0.84	1463	-	132.6	-	53.3	30	6
	-3.5	2.6	2.6	3.9	893	138	16.0	25	2.72	1960	-	131.4	-	374	12	5.2
	-6.5	2.5	2.7	4.8	1045	163	20.9	47	2.92	2515	-	116.7	-	3145	10	1.3
2/06	-0.25	4.0	3.2	3.0	914	158	28.0	57	1.00	741	*768(34)*	61.9	135(63)	9.5	8	3.2
	-0.75	3.1	3.0	1.1	731	123	18.3	35	0	789	*913(132)*	95.9	148(45)	128	10	3.5
	-1.25	3.0	3.0	1.1	629	109	15.2	27	0.29	894	-	96.3	-	203	8	3.8
	-1.75	2.2	2.6	1.3	428	71	10.2	14	0.85	981	-	93.2	-	327	8	4.4
	-2.5	2.7	2.9	1.2	823	129	14.4	26	0	1337	-	95.4	-	729	8	5
	-4	5.0	5.5	5.6	2613	415	28.8	59	0	1802	-	156.9	-	3214	34	9
	-6	5.3	5.0	9.4	3794	569	46.9	104	0	2365	-	165.0	-	4475	8	9
	-7.5	3.0	4.1	3.9	1462	205	18.8	37	0	2310	-	123.5	-	3537	7	6
3/07	**-0.25**	2.5	2.3	5.3	743	85	10.7	26	0.50	496	*1093(519)*	21.3	88(59)	36.0	19	0.6
	-0.75	2.4	2.4	3.1	775	92	8.4	26	0.50	556	*1186(547)*	23.5	69(65)	41.4	16	0.6
	-1.25	2.2	2.3	3.4	860	91	8.8	21	0.50	779	*1319(505)*	26.2	83(80)	645	18	0.2
	-1.75	1.6	1.7	4.5	867	95	7.1	18	0.50	1126	*1410(349)*	36.4	58(30)	1358	18	0.2
	-2.5	1.6	1.9	3.8	856	94	7.6	21	0.40	1172	*1453(294)*	48.0	57(13)	1422	13	0.2
	-4	1.5	2.1	2.8	764	87	7.2	19	0.90	1399	*1690(266)*	48.3	48(0.1)	1417	17	0.2
	-6	1.3	2.1	1.7	1173	122	10.2	24	0.90	1449	*1688(214)*	48.2	48(0.0)	1791	20	0.2
	-9	1.2	1.9	1.7	1129	138	9.4	22	0.60	1577	*1708(115)*	45.6	43(2.1)	920	19	0.2
31/07	-0.25	2.0	2.2	3.5	532	66	17.1	26	0.60	178	*167(17)*	2.8	2.7(0.3)	12.5	39	1.6
	-0.75	1.6	2.2	4.7	816	92	9.5	28	0.60	424	*340(73)*	15.3	15.3(0.7)	13.7	48	0.3
	-1.25	1.7	2.1	3.5	775	86	12.5	31	0.50	515	-	16.7	-	11.6	10	0.3
	-1.75	1.7	2.2	3.6	871	91	9.2	23	0.25	693	-	22.6	-	23.2	11	0.1
	-2.5	1.7	2.2	3.3	827	90	9.3	23	0.50	1016	-	50.7	-	323	9	0.1
	-4	1.7	2.4	2.9	738	82	7.6	19	0.25	1064	-	45.9	-	887	8	0.1
30/08	-0.25	2.6	1.9	3.8	479	61	17.7	29	1.60	182	*165(15)*	11.0	8.5(2.2)	11.9	34	1.2
	-0.75	1.9	1.8	0.8	434	50	8.8	17	0.60	650	*600(84)*	22.6	20.6(1.9)	18.5	44	1.2
	-1.5	1.9	1.8	1.6	541	60	8.0	18	0.40	1082	-	65.4	-	649	14	0.8
	-2.5	1.8	1.9	1.7	632	68	7.5	18	0.60	1537	-	73.1	-	1370	5	0.3
	-4	1.8	2.1	1.4	715	91	7.2	17	0.90	2110	-	78.0	-	2792	6	0.1
	-6.5	1.8	2.1	3.4	921	107	6.4	17	0.90	2175	-	79.0	-	2342	6	0.2
27/09	-0.25	2.6	2.0	3.8	582	72	23.0	38	2.95	209	*218(10)*	2.4	2.4(0.3)	11.6	49	1.6
	-0.75	1.8	1.8	2.3	510	58	10.5	19	0.85	451	*514(67)*	3.6	3.8(0.3)	23.5	99	1.1
	-1.5	1.7	1.8	3.1	611	70	8.5	22	0.35	628	*682(191)*	7.4	7.8(0.3)	17.9	61	1.1
	-2.5	1.8	1.9	3.8	790	87	7.9	22	0.45	961	*913(87)*	51.2	45(5)	34.8	13	0.4
	-4	1.7	1.8	2.7	753	85	6.6	21	0.95	1327	-	61.9	-	607	9	0.1
	-6.5	1.7	2.0	2.7	771	85	4.9	16	0.50	1786	-	73.2	-	1487	8	0.1
	-8.5	1.6	2.0	4.0	785.1	87	4.2	18	0.45	2124	-	71.6	-	1199	8	0.1

Table 5 (continued)

ABER BENOÎT (REFERENCE)																
Date	Depth	Fe-P	Auth-Ca-P	Orga-P	Orga-C	Total N	Chlo a	Phaeopigment	NO_3^-	NH_4^{1}	NH_4^{2}	PO_4^{1}	PO_4^{2}	HS^-	Fe^{2+}	Mn^{2+}
	cm			µmol g^{-1}				µg g^{-1}				µmol l^{-1}				
12/03	-0.25	1.7	2.0	2.4	433	81	8.2	9.1	5.0	32.6	*40.5(7.3)*	3.8	3.13(0.99)	11.3	25	2.2
	-0.75	4.4	2.4	7.4	1317	242	28.0	50.5	2.0	106.3	*100(6.8)*	7.4	12.4(4.33)	9.2	36	1.7
	-1.5	3.2	2.5	4.9	1238	199	21.6	35.6	0.9	93.7		14.0		6.8	32	1.2
	-2.5	2.2	2.2	2.4	900	148	13.3	19.5	0.9	65.3		9.8		10.1	14	0.8
	-4	1.7	2.3	1.5	722	110	11.4	14.3	0.9	49.7		7.9		6.3	10	0.3
	-6.5	1.6	2.4	3.3	828	119	10.5	16.9	22	17.4		3.8		9.5	3	0.3
06/05	-0.25	4.6	2.9	1.6	800	135	11.2	47.2	5.0	73.0	*52.7(22.2)*	10.1	5.63(3.89)	10.1	24	0.8
	-0.75	2.9	2.7	5.3	2856	419	20.0	31.5	1.0	147.9	*134(14)*	12.9	10.4(2.36)	5.4	14	0.6
	-1.5	2.3	2.3	3.5	1157	181	20.7	27.2	0.9	147.9		12.9		9.5	4.0	0.3
	-2.5	1.5	2.0	2.8	751	115	10.6	15.2	0.9	135.7		10.1		55.7	1.0	0.1
	-4	1.3	2.0	2.7	651	102	8.8	12.1	0.9	155.0		9.7		67.3	2.0	0.1
	-6.5	1.4	2.3	2.2	862	131	9.9	14.4	1.0	126.0		8.0		50.9	2.0	0.1
02/06	-0.25	3.3	2.3	1.8	584	92	25.1	16.9	4.0	41.0	*50.3(13)*	5.3	6.13(0.72)	13.7	12	2.1
	-0.75	2.6	2.5	0.0	848	140	16.6	17.8	2.0	118.4	*103(13)*	8.9	9.53(0.55)	5.1	51	1.3
	-1.25	2.3	2.7	1.9	971	173	14.1	22.3	0.9	153.7		6.0		5.1	48	1.0
	-1.75	1.6	5.3	0.0	672	113	10.0	13.5	1.0	156.3		10.1		5.1	5.0	0.5
	-2.5	1.7	3.3	2.5	850	126	12.8	19.7	0.9	176.4		12.3		22.9	5.0	0.4
	-4	1.0	3.6	1.1	404	62	6.2	7.2	0.9	165.4		9.0		22.6	4.0	0.3
	-6	1.1	5.8	0.0	367	56	6.3	6.8	2.0	160.2		5.9		9.5	4.0	0.2
	-7.5	1.0	5.7	0.0	428	58	5.4	6.6	0.0	118.9		3.0		5.1	5.0	0.1
03/07	-0.25	2.5	2.3	5.3	582	78	13.0	17.3	2.0	33.0	*23.3(8.5)*	3.0	2.29(0.62)	13.4	13	0.7
	-0.75	2.4	2.4	3.1	759	94	10.3	13.8	0.7	104.4	*83(20)*	10.9	9.54(1.18)	14.9	26	0.4
	-1.25	2.2	2.3	3.4	712	86	10.7	13.8	0.7	83.2	*87(7.4)*	3.5	5.23(1.45)	10.1	13	0.2
	-2	1.6	1.7	4.5	788	82	16.6	19.4	1.0	74.3	*74(3.3)*	4.7	4.88(0.37)	12.5	14	0.2
	-3.25	1.6	1.9	3.8	424	52	6.5	10.2	1.0	54.9	*54(3)*	1.4	1.93(0.53)	11.3	10	0.2
	-5	1.5	2.1	2.8	483	62	8.5	10.6	1.0	56.6	*55(11.4)*	0.8	0.91(0.16)	10.4	10	0.2
	-7	1.3	2.1	1.7	476	53	5.0	9.0	1.0	31.9	*33.1(5.3)*	0.8	0.84(0.1)	6.8	12	0.1
	-9	1.2	1.9	0.7	478	50	7.9	18.7	1.0	49.6	*46.8(2.6)*	0.9	0.78(0.12)	9.8	13	0.2
31/07	-0.25	2.1	2.1	3.7	486	57	22.8	16.6	5.0	13.4	*15.7(2.1)*	1.0	1.12(0.17)	14.3	7.0	0.2
	-0.75	1.7	2.7	3.2	485	59	12.6	13.5	1.0	48.2	*36.8(9.9)*	5.2	4.65(0.91)	12.8	9.0	0.3
	-1.25	1.7	3.0	2.5	468	62	9.4	11.6	0.9	62.9		4.8		11.6	6.0	0.3
	-2	1.4	4.0	2.6	462	51	7.0	9.1	1.0	100.7		4.6		11.3	4.0	0.2
	-3.25	1.2	4.1	1.8	394	50	5.7	6.6	0.9	120.3		2.5		10.1	3.0	0.2
	-5	1.0	5.6	0.0	385	49	4.8	6.6	1.0	103.8		1.2		8.0	4.0	0.1
30/08	-0.25	2.6	2.1	2.6	494	57	8.2	34.9	3.0	28.1	*25.5(3.6)*	4.2	3.68(0.51)	11.3	9.0	0.2
	-0.75	1.9	2.1	2.4	505	57	9.5	13.6	1.0	95.9	*89.1(5.9)*	10.4	8.94(1.32)	12.8	10.0	0.2
	-1.5	1.7	2.0	2.5	480	51	8.2	11.1	1.0	170.3		11.2		19.9	4.0	0.2
	-2.5	1.7	2.1	3.3	496	48	11.0	14.3	1.0	164.8		6.7		14.6	4.0	0.2
	-4	1.8	2.1	3.0	555	65	9.2	12.7	0.9	235.1		8.2		19.0	5.0	0.2
	-6.5	1.5	2.0	2.1	437	50	6.9	8.2	1.0	180.7		3.1		10.1	9.0	0.1
27/09	-0.25	3.2	2.0	2.8	612	81	32.5	30.5	3.8	32.9	*44.6(15.3)*	5.5	4.72(0.74)	16.4	24	0.4
	-0.75	2.0	1.9	5.2	491	55	13.3	16.6	0.9	76.2	*89.2(20.6)*	5.1	5.36(1.62)	13.4	10	0.3
	-1.5	1.7	2.1	1.4	478	51	9.1	11.1	0.9	90.9	*89.4(1.4)*	4.9	4.79(0.65)	12.5	7.0	0.2
	-2.5	1.4	1.9	0.8	500	53	8.2	9.8	0.9	109.8	*95.3(12.9)*	6.1	6.12(0.19)	18.2	4.0	0.2
	-4	1.4	2.0	2.3	522	62	8.3	11.7	0.8	83.2		4.0		17.0	4.0	0.1
	-6.5	1.4	2.1	1.9	612	73	8.0	13.6	1.7	56.7		2.1		17.9	5.0	0.1
	-8.5	1.5	2.1	4.3	865	96	9.6	16.7	2.0	97.0		3.0		13.4	5.0	0.1

Table 5 (continued)

RIVIERE D'AURAY (OYSTER)																
Date	Depth	Fe-P	Auth-Ca-P	Orga-P	Orga-C	Total N	Chl a	Phaeopigment	NO_3^-	NH_4^1	NH_4^2	PO_4^1	PO_4^2	HS^-	Fe^{2+}	Mn^{2+}
	cm			µmol g^{-1}				µg g^{-1}				µmol l^{-1}				
13/03	-0.25	5.1	2.1	6.9	2467	468	83	86	2.0	125	109(25)	5.3	5(0.7)	3.9	22.0	10.0
	-0.75	4.1	1.9	6.4	1617	310	35	58	1.0	243	242(48)	33.2	35.8(2.9)	6.8	33.0	6.0
	-1.5	2.2	1.5	4.2	2189	436	13	37	1.0	286		39.5		8.0	16.0	3.3
	-2.5	1.6	1.4	4.0	1558	300	7	39	0.1	303		25.3		2.4	6.0	1.5
	-4	1.5	1.4	2.3	1454	273	4	45	0.1	297		22.1		227.1	8.0	1.3
	-6.5	1.4	1.6	3.0	1545	286	2	34	0.0	266		20.8		167.3	12.0	1.2
07/05	-0.25	8.0	2.1	10.4	2238	435	70	144	2.0	193	185(30)	14.4	27(25.8)	9.5	91.0	13.0
	-0.75	7.4	2.2	11.5	2777	518	47	121	2.0	316	322(31)	52.5	70(40.2)	7.7	221.0	14.0
	-1.5	5.9	1.9	10.0	2174	411	31	96	1.0	393		63.8		7.1	212.0	14.0
	-2.5	2.8	1.5	6.2	1750	311	60	57	0.1	415		57.6		8.0	42.0	6.2
	-4	1.9	1.9	6.5	2599	523	106	47	2.0	410		45.2		11.6	9.0	3.5
	-6.5	1.2	1.2	6.5	1534	249	9	37	0.0	309		23.4		87.8	20.0	1.2
6/06	-0.25	2.5	1.0	2.7	1603	295	28	24	2.0	222	214(11)	29.3	28.8(1.1)	7.1	41.0	6.5
	-0.75	3.1	1.6	3.6	1339	244	15	25	3.0	397	407(22)	66.0	57.1(17.1)	2.1	30.0	5.5
	-1.25	2.4	1.3	4.8	1788	302	9	31	2.0	491		88.1		3.9	27.0	4.8
	-1.75	2.9	1.6	3.9	1246	211	8	32	2.0	576		93.4		5.1	12.0	4.6
	-2.5	2.3	1.5	5.4	1324	230	8	27	0.1	565		81.6		12.8	7.0	3.1
	-4	2.0	1.7	6.0	1526	251	4	23	0.0	578		73.8		20.8	4.0	3.3
	-6	1.4	1.0	5.2	1371	233	4	15	0.0	805		105.3		141.4	14.0	2.0
	-8.5	1.1	0.8	2.9	971	166	4	10	0.0	1002		119.7		205.1	9.0	0.7
4/07	-0.25	2.3	1.3	1.1	986	109	12	35	1.0	173	145(25)	27.4	23.3(3.7)	6.0	15.0	8.5
	-0.75	1.8	1.6	4.0	1262	152	11	39	1.0	247	240(7)	48.7	41.2(6.9)	1.5	14.0	4.3
	-1.25	1.9	1.5	6.7	947	116	9	43	1.0	310	314(24)	46.3	40.7(8.0)	9.8	12.0	2.4
	-1.75	2.1	1.7	3.0	870	111	5	36	1.0	351	346(24)	51.1	49.2(3.7)	13.4	19.0	1.6
	-2.5	1.9	1.8	1.7	801	90	6	33	1.0	395	376(19)	51.4	49.1(2.2)	48.8	14.0	0.6
	-4	1.5	1.5	1.7	938	114	4	18	1.0	413	392(25)	41.9	45.5(5.1)	13.7	17.0	0.8
	-6	1.2	1.1	1.1	936	117	5	10	1.0	469	462(37)	43.6	48.0(6.3)	9.5	19.0	0.4
	-8.5	1.1	1.2	3.1	1124	119	2	9	1.0	434	475(36)	37.7	36.4(2.2)	9.8	12.0	0.5
1/08	-0.25	8.6	3.1	7.5	1023	112	7	137	2.0	117	125(25)	4.4	5.2(1.2)	7.7	149.0	6.5
	-0.75	4.9	2.8	6.4	1067	120	6	110	1.0	248	230(49)	19.2	18.9(3.1)	7.7	349.0	6.0
	-1.5	4.0	2.8	6.0	1372	160	6	93	1.0	343		25.4		9.2	258.0	5.5
	-2.5	3.3	2.6	7.1	1562	176	7	83	1.0	438		27.8		7.1	197.0	5.0
	-4	3.0	3.0	6.7	1484	163	5	51	1.5	535		60.5		9.5	18.0	2.5
	-6.5	2.2	1.9	4.5	1250	139	2	21	0.0	888		122.9		24.7	4.0	0.9
31/08	-0.25	11.1	3.2	8.0	2363	330	39	114	2.0	118	114(5)	23.1	20.0(2.8)	8.0	451.0	10.0
	-0.75	4.5	2.0	4.8	2445	338	24	59	1.0	238	218(19)	38.4	34.7(4.7)	14.3	540.0	10.0
	-1.5	3.5	1.8	4.7	2239	286	15	41	1.0	503		105.2		14.3	256.0	10.0
	-2.5	2.4	1.7	3.4	1897	255	13	38	1.0	749		144.2		25.3	10.0	4.0
	-4	1.8	1.6	3.0	2064	257	8	26	1.0	744		93.4		293.2	5.0	1.0
	-6.5	1.3	1.3	2.6	1234	168	4	12	0.0	831		72.4		457.4	7.0	0.2
29/09	-0.25	8.1	2.4	5.7	1671	257	52	106	1.0	161	137(42)	65.0	39.7(22.1)	6.0	108.0	14.0
	-0.75	4.4	2.2	3.4	1725	212	22	83	1.0	342	343(47)	118.4	101.3(15.9	7.7	46.0	10.0
	-1.5	2.0	1.4	1.8	1875	246	13	31	1.0	342		58.8		14.9	6.0	3.1
	-2.5	1.6	1.5	1.3	2271	336	10	32	1.0	282		28.7		33.9	5.0	0.8
	-4	1.1	1.3	2.1	1938	263	9	14	1.0	270		25.9		40.5	5.0	0.4
	-6.5	1.1	1.2	0.5	1515	190	5	10	1.0	274		25.5		14.6	4.0	0.3
	-8.5	0.9	1.7	1.2	1320	161	4	8	1.5	284		25.9		6.0	9.0	0.2

Table 5 (continued)

RIVIERE D'AURAY (REFERENCE)																
Date	Depth	Fe-P	Auth-Ca-P	Orga-P	Orga-C	Total N	Chl a	Phaeopigment	NO_3^-	NH_4[1]	NH_4[2]	PO_4[1]	PO_4[2]	HS^-	Fe^{2+}	Mn^{2+}
	cm			µmol g^{-1}								µmol l^{-1}				
13/03	-0.25	8.8	3.0	10.9	959	165	42	144	11.0	55.1	*47.7(14.5)*	4.3	*3.3(1.1)*	5.4	234.0	27.0
	-0.75	5.5	2.3	6.0	917	163	30	66	2.80	141.5	*144(32)*	21.0	*20.5(2.9)*	8.3	320.0	19.0
	-1.5	3.3	2.5	6.2	740	160	8	61	0.80	156.9		19.4		5.1	112.0	7.0
	-2.5	2.3	2.2	4.5	1824	334	16	45	0.85	192.7		14.4		6.0	32.0	3.1
	-4	1.8	1.7	5.1	682	128	13	28	0.92	292.3		52.8		11.6	10.0	1.3
	-6.5	1.8	2.0	4.2	658	104	3	20	0.85	505.2		66.2		6.3	19.0	0.5
07/05	-0.25	7.1	2.7	8.2	2529	490	77	99	2.80	145.0	*114(30)*	12.0	*8.3(4.7)*	5.4	11.0	10.0
	-0.75	6.3	2.7	4.2	2690	487	62	113	0.80	591.4	*493(95)*	115.5	*94(24)*	25.9	7.0	7.0
	-1.5	4.4	2.8	8.4	2269	434	39	73	0.78	679.0		154.0		78.9	7.0	7.0
	-2.5	3.3	2.7	4.8	1918	334	21	126	0.70	1289.1		216.9		1439.3	8.0	6.0
	-4	4.3	2.5	8.4	1636	305	17	212	0.70	1546.0		218.5		2415.2	7.0	4.3
	-6.5	1.8	1.7	3.6	1496	276	7	51	0.50	1338.0		170.5		1639.9	6.0	1.4
6/06	-0.25	4.7	2.2	7.6	1271	223	11	74	11.7	102.4	*117(13.5)*	10.0	*6.1(3.5)*	5.1	17.0	5.2
	-0.75	3.1	2.0	8.5	1362	240	9	68	14.8	213.1	*236(45)*	31.5	*20.4(9.6)*	3.0	12.0	3.4
	-1.25	2.4	1.9	7.3	1564	290	11	60	2.92	291.0		45.0		6.0	5.0	1.7
	-1.75	2.3	2.2	5.1	1746	329	12	56	0.92	309.9		49.9		23.2	6.0	1.3
	-2.5	2.1	2.1	5.9	2021	373	10	50	0.00	337.9		56.3		5.4	33.0	1.4
	-4	1.4	1.5	2.9	2364	433	8	26	0	427.1		62.6		128.0	15.0	1.3
	-6	1.5	1.4	4.6	2211	395	5	37	0	619.2		76.2		93.5	5.0	1.0
	-8.5	1.5	1.7	8.9	1996	365	3	36	0	673.8		93.6		101.5	7.0	0.5
4/07	-0.25	3.8	1.7	1.2	831	98	16	29	1.0	68.4	*59.8(8.7)*	3.6	*4.6(1.4)*	1.8	101.0	19.0
	-0.75	3.6	2.0	5.2	901	102	14	35	1.0	110.6	*100 (9.1)*	8.8	*8.3(1.1)*	1.5	200.0	16.0
	-1.25	2.4	1.7	1.9	1022	131	8	24	1.0	140.9	*143(10)*	9.2	*12(2)*	5.4	176.0	12.0
	-1.75	1.7	1.7	4.0	1018	164	14	15	1.0	170.6	*178(7)*	13.2	*14(2)*	3.9	61.0	8.0
	-2.5	1.5	1.6	0.0	1026	141	10	16	1.0	191.4		16.1		5.1	14.0	4.6
	-3.5	1.4	1.6	2.2	776	120	5	13	1.0	242.0		23.5		6.8	16.0	2.8
	-5	1.3	1.6	2.8	651	82	3	19	0.9	258.0		28.6		8.3	14.0	2.3
	-7	1.3	1.9	4.3	690	72	3	24	1.0	293.1		23.1		20.2	14.0	1.3
1/08	-0.25	4.1	2.2	5.5	1903	226	66	41	1.9	93.9	*81(13)*	9.1	*8.2(1.1)*	9.2	36.0	5.3
	-0.75	3.9	2.3	3.7	1700	200	43	32	0.9	115.3	*103(13)*	13.3	*11(2.4)*	9.8	20.0	2.9
	-1.5	5.2	2.8	5.2	1671	196	31	35	0.8	221.2		25.0		9.5	43.0	7.0
	-2.5	5.7	2.9	5.6	1573	186	25	35	0.9	325.8		15.5		9.5	13.0	9.5
	-4	4.1	2.6	5.3	1690	215	13	25	3.0	105.2		5.9		9.5	13.0	8.0
	-6.5	2.4	2.2	4.8	1175	132	6	22	3.0	79.7		8.2		9.5	10.0	5.0
31/08	-0.25	3.9	3.2	9.0	2095	281	42	77	1.9	39.2	*49(21)*	2.6	*3.4(2.4)*	3.9	23.0	3.9
	-0.75	3.2	3.4	8.9	1289	169	22	78	1.0	113.6	*127(42)*	11.7	*15.8(8.5)*	9.2	134.0	3.4
	-1.5	3.0	3.3	8.6	984	165	17	66	0.9	250.7		27.9		7.7	224.0	4.6
	-2.5	4.0	3.0	6.5	1182	185	12	78	1.1	359.4		36.5		8.3	153.0	4.4
	-4	2.7	2.9	7.0	1055	142	7	62	1.5	529.8		62.5		14.9	25.0	3.7
	-6.5	1.9	2.2	4.2	830	104	3	33	0.0	793.8		105.3		30.7	5.0	1.7
29/09	-0.25	5.2	2.6	7.3	1443	192	65	76	1.8	4.3	*4.5(2.2)*	2.9	*3.6(0.6)*	5.1	26.0	3.8
	-0.75	3.5	2.5	2.3	1289	168	33	62	0.9	28.7	*30.4(3.8)*	12.3	*12.4(1.6)*	5.4	121.0	3.6
	-1.5	3.1	2.5	9.5	903	113	11	62	0.8	68.9		11.7		5.4	137.0	3.5
	-2.5	3.4	2.9	7.4	969	116	7	70	0.8	218.0		32.4		46.4	232.0	5.0
	-4	3.6	2.6	9.4	775	94	3	62	1.2	414.0		27.2		457.4	146.0	6.1
	-6.5	3.0	2.5	5.5	728	99	2	52	1.2	598.0		95.6		1219.0	21.0	6.6