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Seasonal changes of pCO_2 over a subantarctic *Macrocystis* kelp bed

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Abstract The partial pressure of carbon dioxide (pCO_2), calculated from pH and total alkalinity measurements, was monitored together with chlorophyll *a* and bacterioplankton biomass in shallow coastal water located inside and outside a giant kelp bed (*Macrocystis pyrifera*) situated in the Kerguelen Archipelago, Southern Ocean. In spite of large changes over a short time-scale, pCO_2 variations over the year are large and exhibit a seasonal pattern in which the different stages of the annual biological turnover are well marked. The overall pattern of pCO_2 variations is related to biological activity (development of both photosynthesis and respiration) during almost the whole year. However, physical and thermodynamical constraints exert a strong influence on pCO_2 at meso time-scale (10 days) and/or when biological activity is weak. *Macrocystis* acts to maintain pCO_2 below saturation almost the whole year and large undersaturations (pCO_2 as low as 20 μatm) were observed within the kelp bed. Furthermore, primary production of *Macrocystis* covers a period of $8 \sim 9$ months a year from winter to late summer and the kelp bed seems to favour the spring phytoplanktonic bloom. The buffer factor β indicates that, outside the kelp bed, inorganic carbon dynamics are mainly influenced by air-sea exchange and photosynthesis without calcification. Inside the kelp bed, β suggests calcification by the epiphytic community.

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Introduction

In coastal areas, many factors play a role in the changes of pCO_2. As in the open ocean, warming and cooling of surface water, wax and wane of plankton blooms, wind velocity and lateral advection all influence pCO_2, but other complex processes, such as exchanges with the shallow sediment, outflows of fresh water, tidal mixing and coastal upwellings may strongly affect the carbon budget of the water column (Wollast 1991; Bakker et al. 1996; Frankignoulle et al. 1996a, 1996b; Borges and Frankignoulle 1999). The role of shelf seas in global cycling is indeed still poorly understood (Inoue and Sugimura 1988; Kempe and Pegler 1991; Wollast 1991; Bakker et al. 1996; Frankignoulle et al. 1996a, 1996b; Gattuso et al. 1998; Wollast 1998; Borges and Frankignoulle 1999).

Because of its inaccessibility, the Southern Ocean is the least documented ocean (Metzl et al. 1995; Bakker et al. 1997). With the exception of the works of Metzl et al. (1991), Poisson et al. (1993) and Louanchi et al. (1999), which gave observations above the Kerguelen Plateau, previous studies of pCO_2 in the Southern Ocean did not investigate subantarctic coastal areas. Recently Delille et al. (1997) carried out measurements of pCO_2 and related parameters over diel cycles inside and outside a kelp bed in the Kerguelen Archipelago. However, there is no other study about dissolved CO_2 in the coastal areas of the Subantarctic Zone (SAZ) and Polar Frontal Zone (PFZ).

A substantial proportion of these coastlines is occupied by highly productive giant kelp bed, *Macrocystis pyrifera*. This marine macroalga is one of the largest and grows up to 50 m in length, forming undersea forests in hard-bottom subtidal areas of subantarctic islands (Sfriso et al. 1987; Lavery and McComb 1991; Hanisak 1993). Macroalgae have a great potential for biomass production and CO_2 uptake (Smith 1981; Wilcox and North 1988; Gao and McKinley 1994). Smith (1981) pointed out that the coastal marine macrophytes

ecosystems, including both macroalgae and seagrasses, occupy only about 2×10^6 km^2 but could act as an effective carbon sink because of their biomass (estimated to be about two-thirds of oceanic plant biomass) and relatively high turnover time (about 1 year) compared to phytoplankton (about 1 week). However, with the exception of works of Frankignoulle and Distèche (1984, 1987) and Frankignoulle and Bouquegneau (1987, 1990), little is known about the influence of macrophytes on pCO_2 and their quantitative significance in the global carbon (Gattuso et al. 1998). Moreover, productivity of *Macrocystis* is high and ranges from 1000 to 1300 gC m^{-2} year^{-1} (Mann 1982; Wheeler and Druehl 1986) but Jackson (1977) also measured productivity up to 3400 gC m^{-2} year^{-1} off southern California. Kelps act to reduce currents within the kelp bed and decrease exchanges with surrounding waters (Jackson and Winant 1983). The authors noticed that residence time of water within the kelp bed may be long compared to some biological processes like nitrate uptake by the kelp, phytoplankton doubling and some larval development time. They also pointed out that such reduced currents would allow nutrients to recycle internally and plankton populations to exist solely within. However, in contrast to the numerous studies on the biology and primary productivity of polar microalgae, high-latitude macroalgae have been little studied, although dense populations of highly productive seaweeds are known from the Southern Ocean (Dunton and Dayton 1995).

The purpose of this paper is to examine the seasonal changes of pCO_2 both outside and inside a *M. pyrifera* giant kelp bed, in order to understand the role of physico-chemical and biological processes with regard to pCO_2 within shallow water of the Kerguelen Archipelago, and the influence of *Macrocystis* kelp bed on pCO_2. The present study was undertaken as a part of a program designed to elucidate the annual pattern of pCO_2 in the coastal area of the northern part of the Southern Ocean, as well as the role played by the *Macrocystis* kelp bed with regard to atmospheric pCO_2.

Materials and methods

Sampling

Measurements were carried out from December 1995 to December 1997 in Morbihan Bay (Fig. 1), Kerguelen Archipelago, Southern Ocean (Indian sector). Usually, the Kerguelen Archipelago is cited in the literature as a subantarctic island (Belkin and Gordon 1996; Delille et al. 1997; Razouls et al. 1997). However, from a strict oceanographic point of view, this archipelago is situated either in the PFZ or in the Antarctic Zone, depending on the position of the Polar Front with regard to the island. One should note that this latter position is still a matter of debate (Belkin and Gordon 1996; Park and Gambéroni 1997). Located in the southeast of the archipelago, Morbihan Bay (about 600 km^2) opens to the ocean through the Royal Pass, which is 12 km wide and 40 m deep. The bay is always free of ice. Satellite data processing has permitted estimation of the biomass (wet weight) of *M. pyrifera* at about 1100 kt, spread over an area of about 190 km^2 in the Morbihan Gulf in 1988 (Belsher and Mouchot 1992). Samples were collected

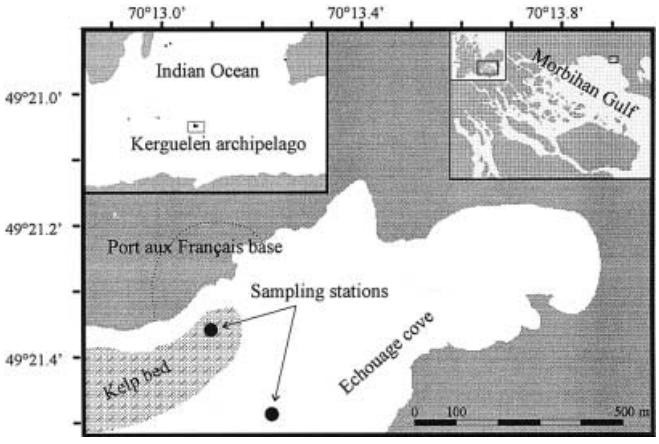

Fig. 1 Location of Morbihan Bay (Kerguelen Archipelago) and sampling sites

in the vicinity of the base of "Port Aux Français" in Echouage Cove (≈400 × 300 m), which is open to dominant winds. Coastlines of the cove are partly surrounded by a *M. pyrifera* kelp bed. Two sampling sites were chosen, one inside and one outside the kelp bed. Both sites were sampled every 10 days, at the same time of the day (between 1.45 p.m. and 2.15 p.m.) in order to reduce the influence of diel cycles. Samples were taken from the surface from the same water mass, and attention was paid to avoid degassing. Analyses were begun in the base laboratory within 30 min after sample collection.

Salinity was determined with a Guildline induction salinometer whose accuracy was 0.003 on the practical salinity scale. Solar radiation and wind velocity measurements were provided by Météo-France.

Inorganic carbon

The inorganic carbon speciation was calculated from pH and total alkalinity (TAlk) measurements. TAlk was measured using the classical Gran electrotitration method on 100-ml GF/F filtered samples. The accuracy of measurements was 4 μeq kg^{-1}. pH was measured using commercial combination electrodes (Ross type, Orion), calibrated according to the NBS scale. The accuracy of pH measurements was 0.01 pH units. CO_2 speciation was calculated using the CO2SYS Package (Lewis and Wallace 1998), the CO_2 acidity constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987), the CO_2 solubility coefficient of Weiss (1974), the borate acidity constant of Dickson (1990a) and the SO_4^{2-} dissociation constant of Dickson (1990b). The total borate molality was calculated using the Uppström (1974) ratio to chlorinity. As silicates and phosphates concentrations were available in 1996 and partially in 1997, they were included in the calculations. Taking into account uncertainties of pH, TAlk, temperature, salinity, silicate and phosphate concentrations, the errors in pCO_2 and DIC were 14 μatm and 9 μmole kg^{-1}, respectively.

Bacterial abundance

Bacterial abundance was determined by acridine orange direct counts (AODC) (Hobbie et al. 1977). A minimum of 300 fluorescing cells with a clear outline and definite cell shape were counted as bacterial cells in 10 random microscope fields.

Chlorophyll

Phytoplankton was studied using chlorophyll *a* concentration. All samples were prefiltered through a 200-μm mesh to remove detritic

material and larger biota, and then filtered by gentle vacuum filtration of 1 l of seawater through a Whatman GF/F glass-fibre filter. The measurements of chlorophyll a were carried out using the spectrofluorometric method developed by Neveux and Panouse (1987). Fluorescence was measured on a Perkin-Elmer MPF 66 spectrofluorometer.

Nutrients

Water samples were filtered through a Whatman GF/F glass-fibre filter. The filtrates were subsequently frozen at −20 °C until laboratory analysis. Nitrate + nitrite, silicate and phosphate concentrations were assayed using a Skalar AutoAnalyser and the method of Treguer and Le Corre (1975). The accuracy of the analyses was assured by calibration with standard salts in low-nutrient seawater. The analytical accuracies were ± 0.1 μmol l^{-1} for nitrate, ± 0.01 μmol l^{-1} for phosphate and ± 0.1 μmol l^{-1} for silicate.

Results

Water temperature (Fig. 2) ranged from 0.7 °C in austral winter (from June to August) to 8.5 °C in summer (from December to March) outside the kelp bed but could reach 15.3 °C within the kelp in calm weather conditions and high irradiancy (Fig. 3). Salinity (Fig. 2) varied between 31.1 and 33.7 and showed drastic changes between two successive samplings. Moreover, even though variations inside and outside the kelp bed tended to correspond, this was not systematic since we observed differences up to 1 on the practical salinity scale between the two sampling sites.

Unfortunately, biological parameters were not wholly available in 1997 and we present here only the results observed in 1996. Chlorophyll *a* concentration (Fig. 4) showed values ranging from 0.4 to 2.1 μg l^{-1} from February to August. In September, an increase occurred inside the kelp bed followed by another sharp and large increase (up to 71 μg l^{-1} inside the kelp bed) 5 weeks later at both sampling sites, when water temperature and solar irradiation were high. Smaller increases occurred in December and January.

Bacterial abundance (Fig. 4) ranged from 7×10^4 to 2×10^6 cells ml^{-1} in 1996. The overall pattern was similar at both sampling sites. Maximal abundance occurred during late summer and autumn (from February to April), but secondary peaks were still observed during winter, in July and August. Bacterial abundance was at its weakest level in spring and early summer (from September to December).

Outside the kelp bed, the concentration of $NO_3^- + NO_2^-$ (Fig. 4) increased progressively from 12 to 29 μmol l^{-1} during autumn and winter. These concentrations decreased drastically in October corresponding to a sharp increase in phytoplankton biomass and reached a low level (3.6 μmol l^{-1}). Depletion was limited in time and concentration of $NO_3^- + NO_2^-$ began to increase just after the phytoplanktonic bloom.

Inside the kelp bed, the overall seasonal pattern was rather similar; however, some small but significant differences existed. A slight decrease in nutrient concentration was initiated in July when solar irradiancy was beginning to increase. Furthermore, decrease of $NO_3^- + NO_2^-$ inside the kelp bed occurred 2 or 3 weeks earlier than outside the kelp bed. This decrease corresponded to the first peak of chlorophyll *a* observed inside the kelp bed in September. In late summer, another sharp depletion of total nitrate and nitrite occurred inside the kelp bed.

pH ranged from 7.94 to 8.46 outside the kelp bed and from 8.07 to 9.11 inside the kelp bed (Fig. 5). At both sampling sites and for the 2 years, pH exhibited similar seasonal patterns with a minimum in winter (May/June) and a maximum in late spring (November) and summer (March). However, it is worth noting that the seasonal pattern was more marked inside the kelp bed, with sharp peaks in summer.

In contrast, TAlk appeared to be constant all year with slight fluctuations ranging from 2.12 to 2.29 (Fig. 5). No clear differences appeared between the inside and outside of the kelp bed.

pCO_2 ranged from 160 to 640 μatm outside the kelp bed and from 20 to 460 μatm inside the kelp bed (Fig. 2). Magnitudes of yearly variations were high (about 350 μatm in 1996 and 450 μatm in 1997) and similar for both sampling sites. Large changes at short time-scales (10 days) were observed. It was possible to distinguish seasonal tendencies in changes of pCO_2. Furthermore, this seasonal cycle for pCO_2 had roughly similar patterns for both sites and both years with a large offset (about 150 μatm) between both sites. However, significative differences in the overall patterns existed between the sampling sites depending on the time of the year. Outside the kelp bed, pCO_2 increased during late summer and autumn (from January to May) whereas strong decrease and undersaturation – atmospheric CO_2 concentrations were estimated to be around 361 ppmV from Amsterdam Island measurement (V. Kazan, personal communication) – were observed within the kelp bed. Nevertheless, maxima of pCO_2 were observed prior to wintertime (July to August) at both sampling sites. With the exception of an increase observed in July 1996, pCO_2 tended to decrease during winter in good agreement with the decrease of temperature, and reached a minimum in August. At the end of winter, when both temperature and solar irradiancy began to increase, pCO_2 tended to increase also. In September a sharp and large decrease of pCO_2 occurred and led to a pCO_2 minimum. Then, pCO_2 increased outside the kelp bed from November to June while other significant decreases occurred inside the kelp bed until April.

Since salinity presented large variations through the year, attention was paid to normalizing DIC to a constant salinity of 35. In the same way as pCO_2, DIC_{35} exhibited large variations at a short time-scale (Fig. 2). However, seasonal tendencies appeared in the DIC_{35} pattern. At both sampling sites, DIC_{35} reached its maximum values during winter and its weakest values in

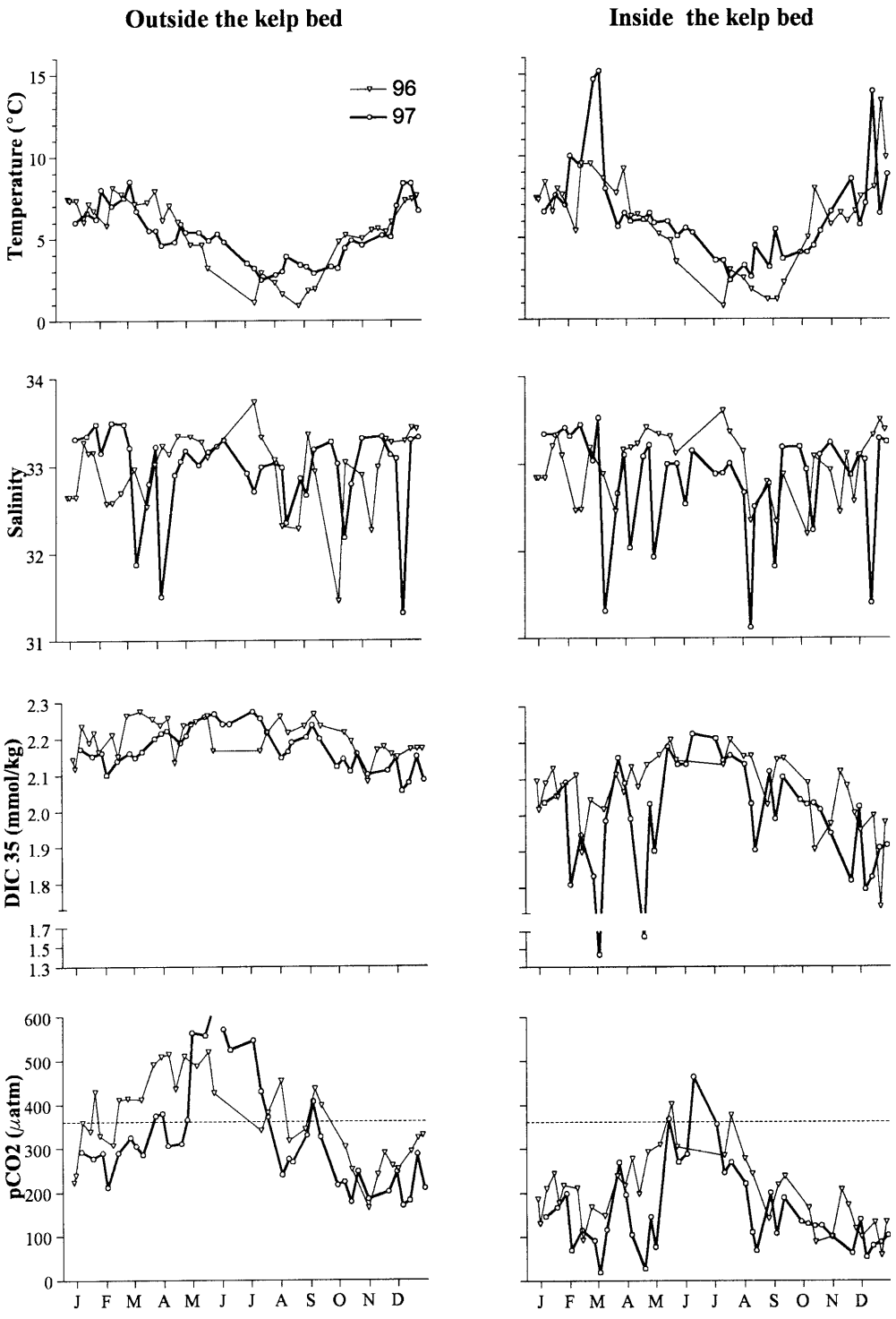

Fig. 2 Seasonal variations of temperature, salinity, DIC_{35} and pCO_2 inside and outside the kelp bed (*thin line with triangles* 1996; *thick line with circles* 1997). The *dotted line* represents the atmospheric pCO_2 value

summer. DIC_{35} exhibited striking differences between the sampling sites. Drawdown of DIC_{35} in spring was larger inside the kelp bed than outside, with a magnitude of yearly variations around 0.2 mmol kg^{-1} outside the kelp bed against 0.5 and 0.7 mmol kg^{-1} inside the kelp bed in 1996 and 1997, respectively. Furthermore, inside the kelp bed variations can be very large, reaching 60 µmol kg^{-1} day^{-1}.

Discussion

Short-term variations

Sudden weather changes, heavy rains, and successions of snowfalls and thaws are very common in the Kerguelen Archipelago. In Echouage Cove, these phenomena

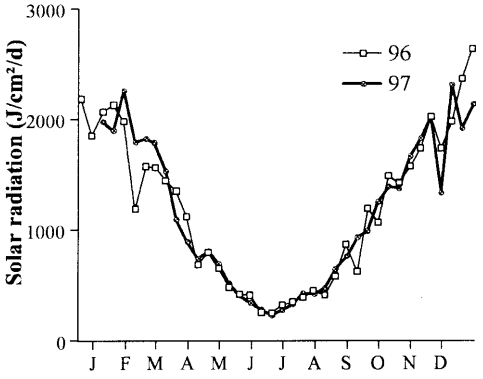

Fig. 3 Solar radiation in Echouage Cove (*thin line with triangles* 1996; *thick line with circles* 1997)

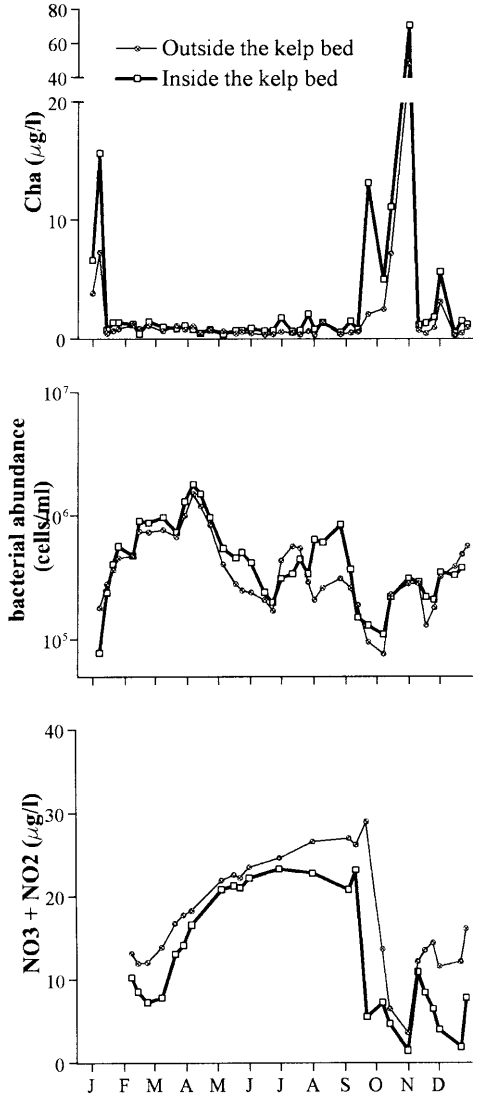

Fig. 4 Seasonal variations of chlorophyll *a*, bacterial abundance and $NO_3^- + NO_2^-$ in 1996 (*thin line with circles* outside the kelp bed; *thick line with squares* inside the kelp bed)

associated with the low rain-water retention of surrounding soils may lead to large and brief inputs of fresh water by rivers and small streams. In contrast, frequent storms and tides favour advection and mixing with offshore water whose salinity is around 33.4 (Razouls et al. 1997). These antagonist processes lead to large short-term variations of salinity. Sudden input of fresh water is responsible for sharp decreases in salinity while mixing with offshore water ensuing storms acts to maintain the salinity of the cove above 33.0.

Furthermore, salinity and temperature differences between inside and outside the kelp bed can reach 1 and 7 °C, respectively. Thus, water within the kelp bed can present a strong heterogeneity with surrounding water in terms of physico-chemical conditions. Some sharp decreases in the salinity patterns occur only inside the kelp bed (Fig. 2), suggesting than after an input of fresh water and subsequent decrease of salinity, the ensuing mixing and increase of salinity are faster outside the kelp bed than inside. This is in accordance with studies by Jackson and Winant (1983), which showed than *Macrocystis* kelp beds counteract advection of surrounding water and slow coastal currents.

The inorganic carbon parameters DIC_{35} and pCO_2 also present large short-term variations and high differences between the sampling sites. Different factors may perceptibly influence inorganic carbon dynamics. Taking into account the TAlk and DIC content of small streams surrounding the cove (TAlk 0.3 meq kg^{-1}, DIC 0.32 mmol kg^{-1}), we calculated that an input of local fresh water corresponding to a decrease in salinity of 1, will decrease pCO_2 and DIC by about 12 µatm and 50 µmol kg^{-1}. Furthermore, physical processes such as exchanges with shallow sediment could have a significative impact on CO_2, but are difficult to assess in the present study.

Furthermore, large short-term variations due to biological activity would not be surprising since biological activity is able to lead to large changes of pCO_2 within a few hours. Poisson et al. (1993) reported pCO_2 daily variations up to 26 µatm in 27 h above the Kerguelen plateau, while Delille et al. (1997) noticed a magnitude of daily pCO_2 variation around 35 µatm in some shallow waters of the Kerguelen Archipelago. In both cases, the authors assumed that biological activity was responsible for such rapid variations. In the same way, previous studies of macrophyte beds showed than water-column pCO_2 may vary greatly over a diel cycle (Smith 1981; Frankignoulle and Distèche 1984, 1987; Frankignoulle and Bouquegneau 1990; Delille et al. 1997).

However, air-sea exchanges tend to maintain pCO_2 near saturation. The effect of air-sea exchanges on the observed pCO_2 is enhanced by the low depth of the cove and by the high wind velocity commonly observed in this area. One can assess the effect of air-sea exchanges on pCO_2 in the cove. The CO_2 air-sea flux (F) can be calculated using the equation $F = \alpha K \Delta pCO_2$ where α is the solubility coefficient of CO_2, ΔpCO_2 the air-sea gradient of CO_2 and K the gas coefficient, which mainly depends on wind speed. Several authors have proposed different algorithms in order to compute K and we applied the two most common algorithms from Liss and Merlivat (1986)

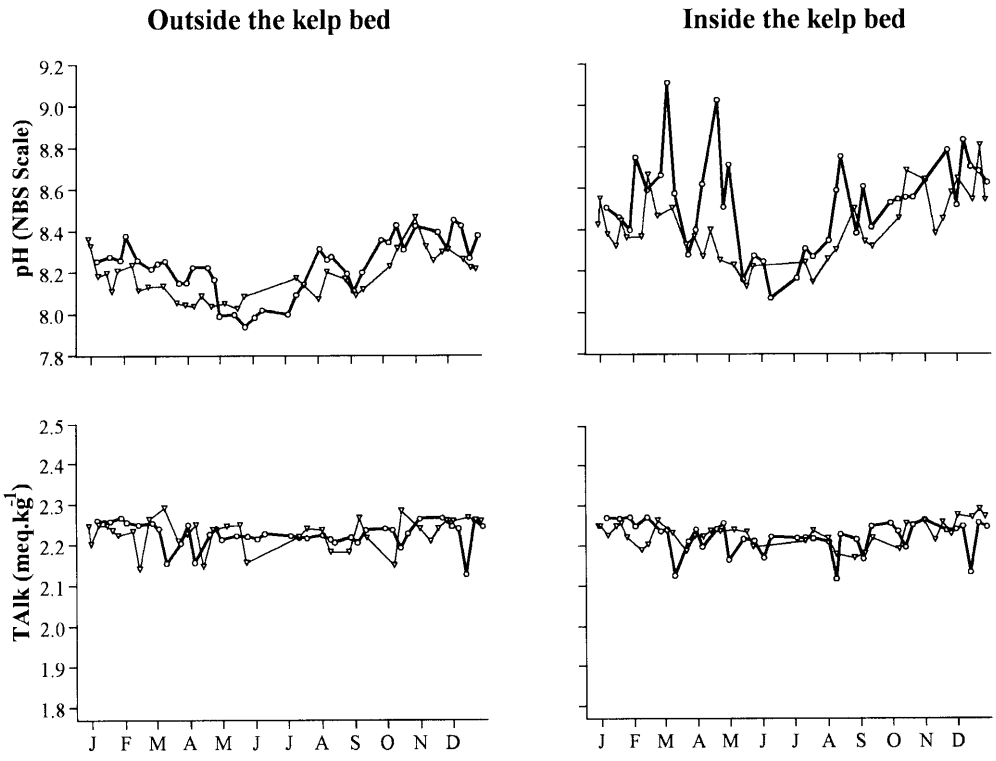

Fig. 5 Seasonal variations of pH and TAlk inside and outside the kelp bed (*thin line with triangles* 1996; *thick line with circles* 1997)

and Wanninkhof (1992). Air-sea flux of CO_2 directly affects the DIC. Taking account of the height of the water column, it is possible to compute the effect of the change of DIC on pCO_2. We computed by iteration (1 day time step) the variation of pCO_2 due to air-sea exchanges in 10 days. In average conditions ($S = 32.9$, $T = 5$ °C, DIC = 2.06 mmol kg^{-1}, wind speed = 9.3 m s^{-1}, water column height = 10 m) with an oversaturation of 100 µatm, air-sea exchanges would lead to a decrease of pCO_2 equal to 29 and 42 µatm, according to the algorithms of Liss and Merlivat (1986) and Wanninkhof (1992), respectively. However, in May 1997 outside the kelp bed, we computed that air-sea exchange would have induced decreases of pCO_2 up to 94 and 127 µatm in 10 days ($S = 33.1$, $T = 5.2$ °C, DIC = 2.14 mmol kg^{-1}, wind speed = 9 m s^{-1}, water column height = 10 m). Thus air-sea exchanges of CO_2 can lead to large changes of pCO_2 over a short time-scale.

In order to explain the large variations in salinity, temperature and inorganic carbon observed at both spatial and short temporal scales, we assume that the shallow water of the cove behaves as follows. Under calm weather conditions advection is weak. Hence, insolation and input of fresh water strongly affect physico-chemical parameters while input of fresh water, exchanges with shallow sediment and biological processes can lead to large changes in DIC_{35} and pCO_2 within the shallow water of the cove. Furthermore, this behaviour is enhanced inside the kelp bed where advection is weaker. When a storm occurs, advection greatly increases. This leads to the homogenization of shallow water, both outside and inside the kelp bed, with offshore water whose physico-chemical parameters, DIC_{35} and pCO_2 are likely to be more constant. Consequently, physico-chemical parameters, DIC_{35} and pCO_2 within the cove tend to mean values. At the same time, air-sea exchange of pCO_2 enhanced by high wind velocity act to maintain pCO_2 near saturation.

Seasonal variations outside the kelp bed

Biological parameters exhibit seasonal patterns, which allow one to distinguish the successive steps of the yearly biological turnover. The phytoplanktonic spring bloom is well marked and leads to a large depletion of $NO_3^- + NO_2^-$ in October. This depletion is limited in time and mineralization starts just after the end of the spring phytoplanktonic bloom. From February to April, bacterial abundance reaches its highest level and the associated strong respiration leads to a large increase of $NO_3^- + NO_2^-$ concentration. This increase is weaker in winter, in good agreement with the decrease of bacterial abundance and subsequent weaker respiration. However, mineralization continues until springtime when the phytoplanktonic spring bloom occurs.

Outside the kelp bed, annual variation of pCO_2 is high (up to 470 µatm). In spite of large variations of pCO_2 over the meso time-scale (10 days), seasonal patterns appear obviously (Fig. 2) and are partly consistent from the 1st year to the next. Hence, although short-term processes exist, they do not mask the seasonal changes.

Considering the merging of the two annual cycles, we discuss the change of CO_2 in June/July 1996 assuming that it was similar to the change in 1997. One can speculate about the effect of physical processes on pCO_2 (fresh water outflow, temperature changes, ventilation). Salinity changes corresponding to inputs of fresh water can induce perceptible changes of pCO_2 (see above) but low salinity events are limited in time and advection with offshore water is likely to quickly counteract the effect of the inputs of fresh water. Therefore, river outflow should have a weak influence on inorganic carbon dynamics over a seasonal scale. For each month, we computed the impact of temperature changes and air-sea exchanges on pCO_2. Impact of temperature changes was calculated using the algorithm of Copin-Montegut (1988, 1989) while effects of air-sea exchanges were computed by iteration (1 day time step) for 30-day periods, taking account of monthly averages of salinity, temperature, DIC, TAlk, atmospheric pCO_2, wind speed, a height of water column equal to 6 m inside the kelp and 10 m outside the kelp and the algorithm of Liss and Merlivat (1986). The use of the algorithm of Wanninkhof (1992) enhances the effect of air-sea exchange but this did not change our analysis. Computation results are presented in Fig. 6. It is worth noting that physical processes (especially air-sea exchange) can potentially exert a strong influence on pCO_2. However, with the exception of late autumn and early winter (May to July) and late spring (November, December), pCO_2 varies in the opposite way with regard to physical constraint. Therefore, the influence of thermodynamical constraints and air-sea exchange on the inorganic carbon system appears to be generally counteracted by other processes during almost the whole year and the explanation of seasonal changes of pCO_2 must be found in the primary influence of biological activity on pCO_2 dynamics.

In fact, the different phases of the yearly biological turnover are distinguishable in pCO_2 patterns. In autumn, pCO_2 increases and reaches its greatest value prior to wintertime. The explanation of the high values reached (520 and 640 μatm) must be the intense mineralization. In early winter, mineralization is weaker, solar radiation reaches its minimum value and, subsequently, photosynthetic activities which are still in process (i.e. kelp bed) are at their weakest. Thus, physical processes are dominant and can exert a strong influence on pCO_2. CO_2 exchanges with the atmosphere, enhanced by strong winter winds, tend to minimize undersaturation or

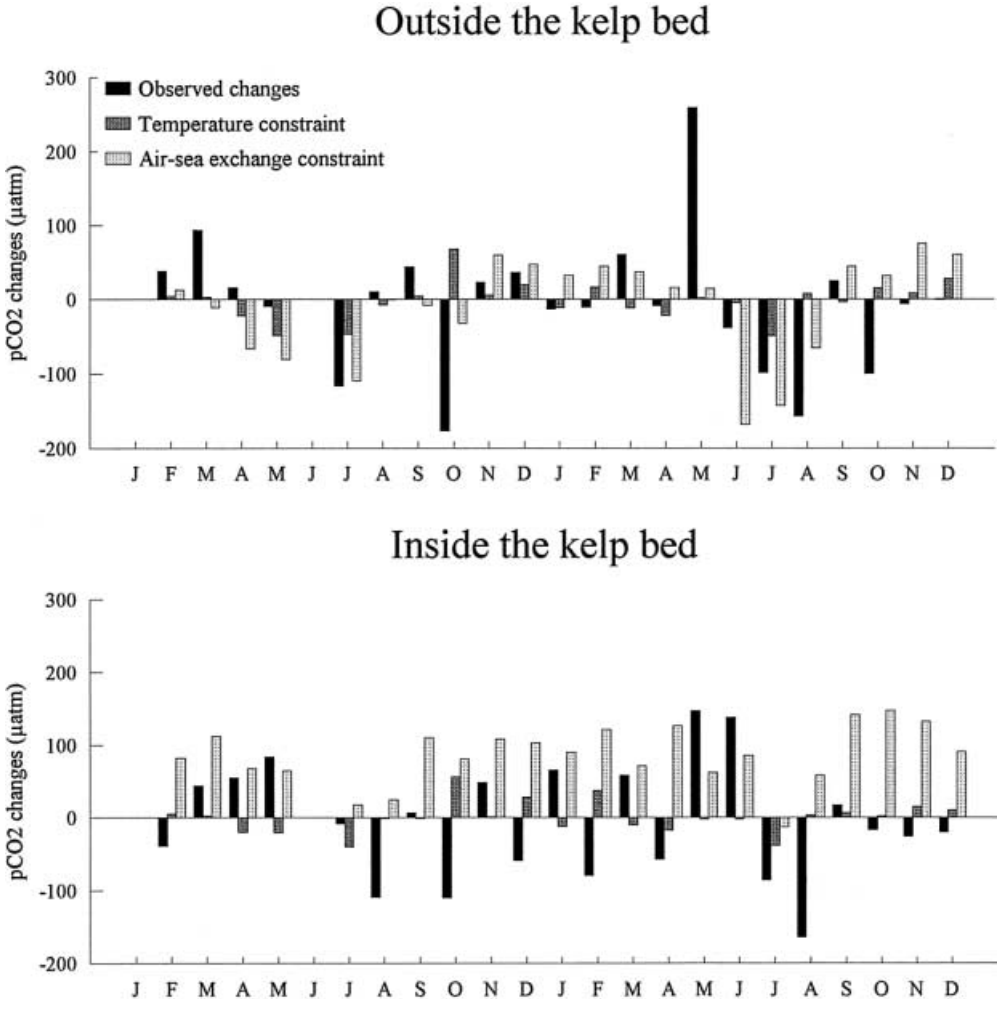

Fig. 6 Monthly pCO_2 changes and assessment of physical forcing (*black bar* observed changes, *dark* and *light grey* pCO_2 changes induced by temperature changes and air-sea exchanges, respectively)

oversaturation and finally reduce pCO_2 during June and July. However, the explanation of ensuing undersaturation at the end of winter 1997 (August) is not obvious. An explanation may be found in the decrease of the temperature of surface water, but the observed decrease of temperature does not account for all the undersaturation. Another reason may lie in the exchange of water of the kelp bed – whose pCO_2 is low – with surrounding water. In September 1997, oversaturation of pCO_2 could be linked to an increase of bacterial abundance. This would suggest a close coupling between bacterial abundance and pCO_2 in the shallow waters of the cove.

In spring, a marked decrease of pCO_2 corresponds with an increase of chlorophyll a biomass and a sharp drawdown of nutrient content. This is the beginning of an intense photosynthetic production, which leads to a minimum value of pCO_2 during the phytoplanktonic bloom. This period is brief, and then pCO_2 starts to increase, with the beginning of mineralization. Furthermore, this increase could be enhanced by air-sea exchange in November and December (Fig. 5).

DIC_{35} shows a consistent pattern with the pCO_2 pattern. Increase of DIC_{35} in autumn can be related to the decay of organic matter. In winter, changes of DIC_{35} are weak in spite of a large decrease of pCO_2. This suggests a low mineralization and a strong influence of some physical processes on pCO_2 (i.e. temperature decrease and advection of offshore water). In summer, as one would expect, the DIC_{35} minimum corresponds to the maximum of chlorophyll a biomass and highlights the influence of primary production on inorganic carbon dynamics.

Influence of the *Macrocystis* kelp bed

Overall patterns of biological parameters are similar at both sampling sites. However, it is interesting to note that the phytoplanktonic bloom and subsequent decrease of $NO_3^- + NO_2^-$ occur 2 or 3 weeks earlier inside the kelp than outside. Thus the kelp bed appears to favour the phytoplanktonic bloom. The reason is not obvious and might lie in lower turbulence inside the kelp bed. However, other explanations cannot be excluded.

The seasonal trend of the CO_2 content of water inside the kelp bed (Fig. 2) shows significant differences with regard to the seasonal pattern of pCO_2 outside the kelp bed. It is essential to pay careful attention to these, taking account of the differences in nutrient contents, since they allow specific biological activity of the kelp bed to be distinguished.

Similarly to outside the kelp bed, Fig. 6 shows that with the exception of autumn (March to June), November 1996 and January 1997, pCO_2 varies in the opposite way to physical constraint. Furthermore, even if pCO_2 varies in the same way as physical constraint, this does not account necessarily for the whole change (May to July 1997). Since the effect of input of fresh water does not exceed a decrease of about 25 μatm (for a salinity decrease of 2), the only explanation for the large undersaturation of CO_2 observed in August ($80 \sim 150$ μatm) must be found in the photosynthetic activity of the *Macrocystis* kelp bed, which would correspond to an increase of solar radiation. Uptake of nutrient attendant to this photosynthetic activity is noticeable in the decrease of nutrient that occurred in July and August despite the high bacterial abundance (Fig. 4). By the end of September, phytoplanktonic blooms begin and induce a strong decrease in pCO_2 and a first depletion of $NO_3^- + NO_2^-$. Photosynthetic production of the kelp bed is then likely to decrease, due to limitation of nutrient (Jackson 1977) and decrease of light availability by phytoplankton and epiphyte communities. Hence, just after the bloom, at a lower photosynthetic activity of the kelp, physical constraints (i.e. air-sea exchange, increase of temperature, advection) lead to a slight increase of CO_2 enhanced by the beginning of mineralization. When $NO_3^- + NO_2^-$ content reaches a sufficient level, together with a high solar irradiation (Fig. 3), photosynthetic activity of the kelp bed increases again and leads to a second marked decrease of pCO_2 and $NO_3^- + NO_2^-$ concentrations. This decrease occurs in contrast with outside the kelp bed where pCO_2 and $NO_3^- + NO_2^-$ continue to increase until winter. It is worth noting that photosynthetic activity of the kelp bed in summer can lead to a value of pCO_2 as low as 20 μatm. On the whole, this photosynthetic activity continues almost all year and maintains pCO_2 inside the kelp bed below saturation from July to May.

Kelp bed primary production yields to substantial decrease of DIC_{35}. Overall decrease of DIC_{35} is initiated in August, suggesting that kelp bed primary productivity begins as soon as solar irradiancy increases. In spite of homogenization with surrounding water, primary production of the *Macrocystis* kelp bed acts to maintain the DIC_{35} value within the kelp bed below the value observed outside the kelp from August to April. This leads to an estimate than primary production of the kelp bed covers a period of $8 \sim 9$ months a year. Moreover, it is worth noting that inorganic carbon uptake by *Macrocystis* was large enough to yield decreases of DIC between 30 and 60 μmol kg^{-1} day^{-1}. Taking into account the depth of the kelp bed ($5 \sim 6$ m), these decreases would correspond to a productivity between 2.2 and 4.2 gC m^{-2} day^{-1}. These rough values are in the range of previous observations of productivity of *Macrocystis* (2.7–3.6 gC m^{-2} day^{-1}) in warmer water (Mann 1982; Wheeler and Druehl 1986). However, our calculations are biased by mixing with surrounding water. In fact, daily uptake of DIC within the *Macrocystis* kelp bed of the Kerguelen Archipelago can be larger – up to 100 μmol kg^{-1} day^{-1} – as was reported by Delille et al. (1997). Therefore, study of DIC_{35} variations over diel cycles – weaker influence of mixing – is needed to improve measurement of *Macrocystis* productivity.

This primary production yields to undersaturation of CO_2 during almost the whole year. Thus, the

Macrocystis kelp bed would act as a strong sink of CO_2. However, accurate study of the role of the kelp bed with regard to the atmosphere would need to take account of the diel cycles of pCO_2 within the kelp bed, as well as computation of CO_2 fluxes.

Buffer factor

The homogeneous factor [$\beta = d\ln(pCO_2)/d\ln(DIC)$] is a useful tool for identifying processes that mainly affect the inorganic carbon dynamics, such as primary production or water mass mixing. It can be obtained by plotting $\ln(pCO_2)$ versus ln(DIC), and when dissolved CO_2 is the only inorganic species involved in the carbon exchange (e.g. air-sea exchange), β corresponds to the Revelle factor and its value is about 12 for average seawater conditions. However, this value depends also on the processes that induce modifications of the inorganic species involved in the CO_2 system speciation. Thus, if organic matter production/respiration by organic metabolism have a weak effect on β, this value can decrease down to −7 when inorganic metabolisms develop (e.g. uptake or release of bicarbonates and/or carbonates by calcifying organisms). When organic and inorganic carbon metabolisms occur simultaneously, one can use the relation $\beta = -7.02 + 0.186 \times \%C_{org}$ (Frankignoulle 1994) where $\%C_{org}$ is the percentage of change in inorganic carbon concentration due to organic metabolism (photosynthesis and respiration). Hence, we can assess the influence of inorganic metabolism on the inorganic carbon dynamics.

By using this approach, Robertson et al. (1994) studied a coccolithophore bloom in the North Atlantic while Wanninkhof and Feely (1998) discussed the influence of the aging water masses from the Atlantic to the South Indian and South Pacific Oceans. Furthermore, the buffer factor may provide substantial help in assessing inorganic carbon dynamics even in coastal waters where complex processes develop (Frankignoulle et al. 1996b, 1996c).

The data set presented here allows us to estimate β values using the slope of a plot of $\ln(pCO_2)$ versus ln(DIC). To remove influence of temperature and salinity, pCO_2 were computed from normalized TAlk and DIC ($TAlk_{35}$ and DIC_{35}) for a constant temperature $T = 5$ °C. Then, we plotted this value [$pCO_{2(35,5°)}$] as a function of DIC_{35}. Figure 7 illustrates results obtained using the whole data set from the monitoring and gives the relationship between $\ln[pCO_{2(35,5°)}]$ and $\ln[DIC_{35}]$ for both sampling sites.

It is worth noting that in spite of large variations of physico-chemical conditions (i.e. pH, DIC_{35}, temperature and salinity) and the length of the monitoring (2 years), $\ln[pCO_{2(35,5°)}]$ versus $\ln[DIC_{35}]$ exhibit fairly good linear relationships at both sampling sites. Outside the kelp bed, the slope, β, is calculated to be 12.61 ($r^2 = 0.82$). This value is close to the expected theoretical value ($\beta = 13.2$, with $S = 32.96$, pH = 8.21, TAlk = 2.23 mmol kg^{-1}), obtained from average values observed during the 2 years and calculated assuming that dissolved CO_2 is the only inorganic species involved in CO_2 dynamics. This observation clearly indicates that total inorganic carbon variations measured in this area are mainly driven by changes in the dissolved CO_2 level, e.g. air-sea CO_2 exchanges and/or organic matter production/degradation, without any associated calcification or calcium carbonate precipitation.

Inside the kelp bed, $\ln[pCO_{2(35,5°)}]$ versus $\ln[DIC_{35}]$ exhibit a quite linear relationship. This suggests that some processes within the kelp bed exert a strong constraint on the behaviour of the carbonate system and that the triggering due to hydrodynamic processes is partially hidden over the year. In fact, residence time in the interior of the kelp bed is likely to allow biological processes that develop within the kelp bed to exert a strong influence on characteristics of water masses flowing through the kelp bed, accordingly to the observations of Jackson and Winant (1983).

A preliminary calculation inside the kelp bed gives $\beta = 9.08$ ($r^2 = 0.95$), which differs significantly from the result outside the kelp bed. In spite of a good correlation coefficient in calculation of the relationship, $\ln[pCO_{2(35,5°)}]$ versus $\ln[DIC_{35}]$ displays a slight curve, allowing us to think β is not absolutely constant throughout the year. If one divides the year between

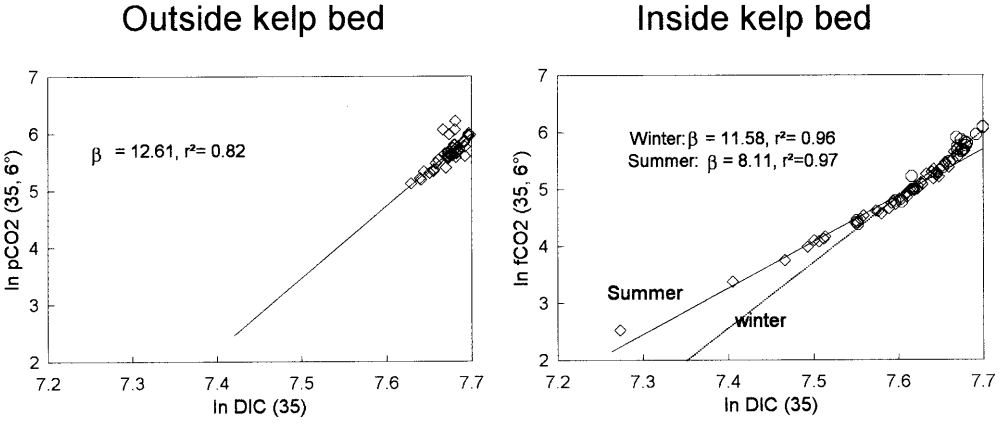

Fig. 7 Plots of $\ln[pCO_{2(35,6°)}]$ versus $\ln[DIC_{35}]$ and regression lines to obtain the homogeneous buffer factors. On the *left* figure, *squares* and *thin line* correspond to both years. On the *right* figure, we distinguish summer (*squares* and *thin line*) and winter (*circles* and *dotted line*) seasons

winter (May to August) and the other seasons, calculations give $\beta = 11.58$ ($r^2 = 0.96$) in winter and $\beta = 8.11$ ($r^2 = 0.97$) for the rest of the year. In winter, β is close to the value outside the kelp bed, indicating that total inorganic carbon variations are mainly driven by changes in the dissolved CO_2 level, e.g. air-sea CO_2 exchanges and/or organic matter production/degradation. Decrease of β in summer lies in the removal of CO_3^{2-} and/or HCO_3^- superimposed on changes of the CO_2 concentration. Two processes might be responsible for such removal: (1) uptake of HCO_3^- by the *Macrocystis*, (2) calcification by the epiphytic community (uptake of CO_3^{2-} and/or HCO_3^-).

A number of macroalgae are reported to be capable of using HCO_3^- (Gao and McKinley 1994). However, if *Macrocystis* uses HCO_3^- for growth, large uptakes of DIC – up to 60 μmol kg^{-1} day^{-1}, which have been observed – would lead to weak changes of pCO_2 (less than 15 μatm day^{-1}) and large changes of TAlk, which are not observed in the present study, and also in the study of Delille et al. (1997), whose reported daily decrease of DIC of 90 μmol kg^{-1} day^{-1} associated with decreases of pCO_2 of 220 μatm above some *Macrocystis* kelp beds of the Kerguelen Archipelago. This leads us to think that *Macrocystis* uptake of HCO_3^- is weak or non-existent. Therefore, the explanation of the decrease of β must be found in the presence of calcifying organisms which develop within the kelp bed. This is in accordance with the presence of small shells on the fronds of *Macrocystis* in the Kerguelen Archipelago. Moreover, other epiphyte species probably remove CO_3^{2-} and/or HCO_3^- in substantial amounts.

Conclusions

In spite of an important temporal variability at meso time-scale, partly due to hydrodynamical processes, pCO_2 in the shallow water of the Kerguelen Archipelago exhibits obviously large seasonal changes. These changes are mainly influenced by biological activity almost the whole year. Photosynthesis in spring and summer is responsible for marked undersaturation of CO_2 while decay of organic matter leads to oversaturations in autumn and winter. Physical processes have a great potential to influence pCO_2 but, with the exception of winter time, influences of temperature variations and air-sea exchanges are hidden by the magnitude of variations due to biological processes. Thermodynamical constraints and air-sea exchanges play a leading role in inorganic carbon dynamics in winter when biological activity is weak, as well as between the end of the phytoplanktonic spring bloom and autumnal mineralization. Furthermore, physical processes (i.e. input of fresh water, advection and air-sea exchanges) exert a strong influence on CO_2 and DIC at meso time-scale.

Primary production of *Macrocystis* appears to cover a period which extends from winter to late summer and favours the development of the spring phytoplanktonic blooms. Growth of macrophytes tends to act as a net sink for atmospheric CO_2 almost the whole year and leads to very low values of pCO_2 (as low as 20 μatm).

In our approach, we used the homogeneous buffer factor (β) to discuss processes responsible for the observed CO_2 variations. Plotting $\ln[pCO_{2(35,6°)}]$ versus $\ln[DIC_{35}]$ yields excellent relationships, even in such a complex system and for a long time (2 years). Outside the kelp bed, inorganic carbon dynamics seem to be mainly driven by air-sea exchanges, physical processes and organic production without calcification. CO_2 uptake is likely to be the major pathway for inorganic carbon assimilation by *Macrocystis* while inorganic epiphytic metabolism appears to develop within the *Macrocystis* kelp bed in summer.

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