CO_2 chemistry in the water column above a posidonia seagrass bed and related air-sea exchanges

CO_2/pH
Seawater
Posidonia
Air-sea exchanges
Buffer factor

CO_2/pH
Eau de mer
Posidonies
Échanges air-mer
Pouvoir tampon

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ABSTRACT

An often sinusoidal diel pH signal is detectable at −0.5 m and −8 m above a *Posidonia oceanica* (L.) Delile seagrass bed (Bay of Calvi, Corsica). Total alkalinity, temperature and pH measurements permit description of the CO_2 chemistry in the 8 m water column, and its daily and yearly fluctuations.

The homogenous buffer factor [($\beta = \partial \ln PCO_2$ water/$\partial \ln \Sigma$ CO_2)] and the physico-chemical buffer factor [($\beta' = \partial \Sigma$ CO_2 water/∂pH)] are calculated and shown, as expected, to depend essentially on temperature and mean pH.

The yearly variation of total alkalinity shows a sudden drop (0.06 meq./l) during summer, which most probably finds its explanation in the sudden increase of activity of Melobesiae epiphytes. However, carbonate losses and gains in the water column are balanced out over a yearly period. The mean pH is lowest in June-July. 90% of the corresponding maximum acidification is explained by the temperature increase and the total alkalinity diminution.

CO_2 diel oscillation is largest close to the annual acidity maximum, and drops to zero in winter, accurately reflecting the biological activity of the seagrass bed. The corresponding Σ CO_2 change permits estimation of the net production and respiration rates of the total ecosystem.

Net production at its highest is 5.3 g C $m^{-2} d^{-1}$ in agreement with observations by Bay (1978).

Air-sea CO_2 exchanges were measured while monitoring the CO_2 chemistry in the water column. The observed out-fluxes vary considerably from hour to hour. Mean values show a yearly maximum in summer (mean September $F_0 = 11.7 . 10^{-6}$ mg Co_2 $cm^{-2} min^{-1}$), but there is no flux during winter and an influx has so far never been measured.

The atmospheric partial CO_2 pressure is 325-330 ppm. It would appear that the reentry of CO_2 into the sea requires $\beta = 10$ at pH = 8.29, $t = 12°C$, PCO_2 water = 300 ppm (lowest observed β value is 10.45, pH 8.23, $t = 11.8°C$, PCO_2 water = 360 ppm). Slight overpressure (25 to 50 ppm) appears to be required to force the surface microlayer. The whole Posidonia belt in the Mediterranean basin may be considered as a CO_2 emitter which ceases in winter and is modulated by the ecosystem photosynthesis and respiration, temperature and sea-state.

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RÉSUMÉ

Chimie du CO_2 dans la colonne d'eau au-dessus d'un herbier à posidonies et échanges air-mer correspondants

Une variation nycthémérale de pH, souvent presque sinusoïdale, peut être enregistrée à −0,5 et à −8 m, au-dessus de l'herbier de posidonies (*Posidonia oceanica* (L.) Delile) dans la baie de Calvi (Corse). L'alcalinité totale, la température et le pH permettent de décrire la chimie du CO_2 dans la colonne d'eau de 8 m au-dessus de l'herbier, sa fluctuation journalière et sa variation annuelle. Le pouvoir tampon homogène ($\beta = \partial \ln PCO_2$ eau/$\partial \ln \Sigma$ CO_2) et le pouvoir tampon physico-chimique ($\beta' = \partial \Sigma$ CO_2/∂pH) ont été calculés, et s'avèrent comme prévu déterminés essentiellement par la température et le pH moyen.

La variation annuelle d'alcalinité totale présente une chute brusque (0.06 méq./l) en été, et trouve plus que probablement sa cause dans la croissance soudaine d'épiphytes (Mélobésiées). Cependant, les gains et pertes en carbonate de la colonne d'eau s'équilibrent sur un an. Le pH moyen est minimum aux mois de juin-juillet. 90% de l'acidification correspondante s'expliquent par l'augmentation de la température et la baisse d'alcalinité totale. L'oscillation nycthémérale de CO_2 est la plus élevée au voisinage du maximum d'acidité annuel et tombe à zéro en hiver. Elle reflète parfaitement l'activité biologique de l'herbier. Les variations de Σ CO_2 permettent d'estimer la production et la respiration nette de l'ensemble de l'écosystème. La production nette à son maximum est de 5.3 g C $m^{-2}j^{-1}$, en accord avec les observations de Bay (1978).

Les échanges air-mer de CO_2 ont été mesurés pendant qu'étaient suivies les fluctuations du pH dans la colonne d'eau.

Les flux sortants observés varient d'heure en heure. Les valeurs moyennes présentent un maximum annuel en été (F_0 moyen en septembre = $11.7.10^{-6}$ mg CO_2 $cm^{-2}min^{-1}$), mais il n'y a pas de flux en hiver, et jamais un flux entrant n'a été jusqu'à présent enregistré. La pression partielle de CO_2 dans l'air est de 325-350 ppm. La réentrée de CO_2 dans la mer devrait, semble-t-il, se faire à $\beta = 10$ (soit à pH = 8.29, $t = 12°C$, PCO_2 eau = 300 ppm; la valeur expérimentale la plus basse pour β est 10.45, pH 8.23, $t = 11.8°C$, PCO_2 eau = 360 ppm).

Une légère surpression (25 à 50 ppm) paraît nécessaire pour forcer la microcouche de surface. L'entièreté de la ceinture de posidonies du bassin méditerranéen doit être considérée comme un émetteur de CO_2 qui s'arrête en hiver et qui est modulé par la photosynthèse et la respiration de l'écosystème, la température et l'état de la mer.

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INTRODUCTION

In situ measurements to evaluate CO_2 transfer at the air-sea boundary and CO_2 variations within the water column are difficult to carry out and to interpret. Not only an exact and coherent knowledge of the CO_2 chemistry in seawater required but also an understanding of chemical and biological processes linked to diel or seasonal cycles and random events or phenomena appearing as such to the local observer: plankton patchiness and vertical migrations, sea-state, advection, turbulent diffusion.

The relative intensity of the CO_2 signal produced by a Posidonia sea-grass bed (*Posidonia oceanica* (L.) Delile) such as that studied in the Bay of Calvi (Corsica), permits the elimination of iost of the difficulties related to plankton, and the concentration of attention on the regular diel signal of the Posidonia (respiration, photosynthesis). Advection may be neglected in first approximation during each short campaign of measurements at regular intervals during the year; preliminary measurements show that horizontal CO_2 gradients are small above the Posidonia seagrass bed, which covers 10 km^2 in the Bay of Calvi, our measurements being made at its coastal limit. The observed water column (8 m) is well mixed (S, $t°$ constant over depth). Continuous records of the pH changes below the surface and directly above the seagrass bed and alkalinity determinations were used to calculate the speciation of carbonic acid and the internal buffer factor. The Σ CO_2 changes were used to evaluate net global productivity and respiration.

Air-sea exchanges have been measured (floating bell, I. R. spectrophotometry), and an attempt to correlate these results with events in the water column is presented.

MATERIAL AND METHODS

All the results presented here concerning the speciation of inorganic carbon in seawater were calculated from pH and total alkalinity measurements. Direct Σ CO_2 controls were carried out under laboratory conditions.

pH measurements

The pressure compensated sea-going glass electrode cell described by Distèche (1959; 1962; 1964; 1974) and Distèche and Dubuisson (1960) is used. The electrode is built to minimize junction potentials and gives an extremely stable electromotive force, which permits the detection of 0.001 pH unit variations (the glass electrodes, glass stem and bulb are provided by Kent Industrial Measurements Ltd, UK). Various methods have been tested to calibrate the electrodes. Best results were obtained by titrating a solution of Na_3PO_4-NaCl 0,649 M (S = 38 $^0/_{00}$, *in situ* conditions) with hydrochloric acid, covering a pH span of about 5 pH units (pH 3-8.5). Careful analysis of the curves and verifica-

tion of the values obtained for each dissociation constant make it possible to measure the Nernst slope of the electrode and to determine whether it is pH dependent or not. The absolute value of pH can finally be measured within 0.01 pH unit.

Laboratory tests were made to check the coherence of our pH measurements with a chosen set of dissociation constants for carbonic and boric acid established on the basis of the NBS pH scale (Mehrbach et al., 1973; Lyman, 1957, cited by Millero, 1979 and by Hansson, 1973). Known amounts of Na_2CO_3 dissolved in 0.649 M NaCl and of CO_2 saturated 0.649 NaCl solutions were added to seawater, showing excellent agreements with the calculated values.

Alkalinity and Σ CO_2 measurements

The titration method proposed by Gran (1952) is used to measure total alkalinity. After degassing the sample, pH is measured at seven pH intervals beyond the equivalence point. The extrapolation of the Gran function [$\varphi = (V_{HCl} + V_{sample}).10^{-pH}$ versus V_{HCl}] to zero value gives V_{HCl} at the equivalence point. The precision is about 0.2%. Weak acids other than boric acid can be neglected in all the experiments described in this paper.

Σ CO_2 checks are carried out by degassing a seawater sample after acidification and carrying the CO_2 in a nitrogen flow through an I.R. spectrometer (*see* below; precision: 0.4%).

Atmospheric CO_2 and air-sea CO_2 exchange measurements

To measure the atmospheric CO_2 level, an infra-red gas analyser is used (Miran 1-F type). Field and laboratory calibrations are made using nitrogen-CO_2 mixtures of known CO_2 content available on the market (352 ± 11 ppm and 297 ± 9 ppm CO_2).

To determine the direction and the magnitude of the CO_2 flux at the air-sea interface, a plastic floating bell system is used (Fig. 1). The exchange surface is 1.13 m^2 and the volume of the closed circuit is 0.350 m^3. When the circuit is closed, the initial variation of partial CO_2 pressure gives both magnitude and directions of the flux. When open it permits measurement of the atmospheric CO_2 level at 50 cm above the sea surface. We have verified the stability of the I.R. analyser in absence of any flux. The method appears to be very sensitive to relative variations of the CO_2 partial pressure (limit of flux detection $< 1.10^{-6}$ mg CO_2 $cm^{-2} min^{-1}$).

Calculations

The speciation of carbonic acid is calculated following the method described by Millero (1979), using the dissociation constants as indicated in 2.1, corrected for salinity and temperature and the coefficient of solubility of CO_2 in seawater given by Weiss (1974). The concentration of borate is calculated as usual from the ratio S ‰ (total borate) given by Culkin (1965).

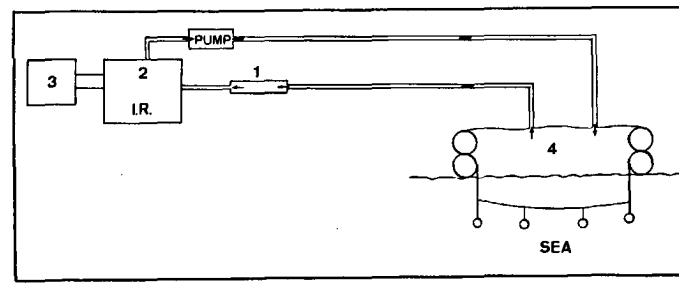

Figure 1

Plastic floating bell system to measure sea-air CO_2 exchanges. After draining the system with surface air, and subsequently closing it, the initial change of partial CO_2 pressure permits the estimation of both direction and value of the flux (1: silicagel; 2: infra-red gas analyser; 3: recorder; 4: plastic floating bell).

Système de cloche flottante pour mesurer les échanges air-mer de CO_2. Après avoir purgé le système avec l'air de surface, et l'avoir isolé, la variation initiale de la pression partielle en CO_2 permet d'estimer le sens et la valeur du flux (1 : silicagel; 2 : analyseur infra-rouge; 3 : enregistreur; 4 : cloche flottante).

The precision of the speciation calculations is of the oder of 0.3% for bicarbonate, 2% for carbonates and 3% for dissolved CO_2.

RESULTS AND DISCUSSION

Diel and yearly CO_2 species changes in a 8 m water column above a Posidonia seagrass bed; buffer factor; ecosystem productivity

Figure 2 shows that the Posidonia seagrass bed generates a very regular pH signal in the water column, correlated to the dissolved oxygen variations and solar radiations as shown by Wehren *et al.* (1981).

Similar signals were observed at nearly monthly intervals during 1980, 1981 and 1982. Their height is illustrated further in Figure 4 where they are rearranged to cover a single year.

The diel changes recorded during September 1981 and plate April-early May 1982 are taken as examples (Fig. 2). The surface pH (—50 cm) and the bottom pH were continuously recorded over a period of several days. Within this short time interval, the total alkalinity remains at a constant value (measured every three hours) and the temperature difference between day and night does not exceed 1°C. The temperature difference between surface and bottom is rarely greater than 0.5°C.

Table 1 gives the concentrations of the different inorganic carbon species calculated at the pH maximum and minimum. The water column is well mixed: the surface signal is only slightly attenuated and out of phase with the bottom one. The calculations of the vertical turbulent diffusion coefficient will be discussed in another paper. The values obtained are of the order of $10^{-2} m^2 sec.^{-1}$.

The buffer factor which expresses the CO_2 species changes in seawater as a result of internal variations such as those related to the global biological activity of a seagrass bed or from exchanges at the sea-air interface is generally defined as $\beta = (\partial P/P)/(\partial \Sigma/\Sigma)$

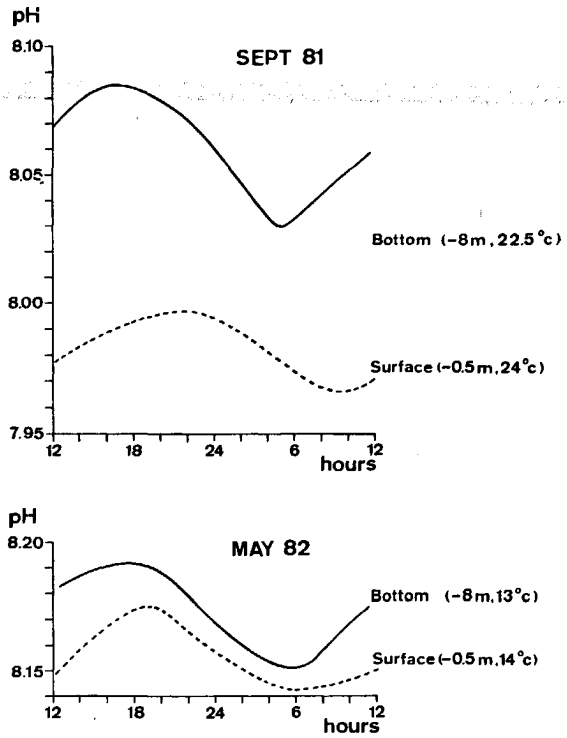

Figure 2

Recorded pH near the surface (—50 cm) and at —8 m (bottom) in September 1981 and in April-May 1982. The signal corresponds fairly well to the biological activity. Surface signal is slightly attenuated and out of phase in comparison with the bottom one. The system is clearly more turbulent in April-May.

pH mesuré près de la surface (—50 cm) et à —8 m (fond) en septembre 1981 et en avril-mai 1982. le signal correspond très bien à l'activité biologique. Le signal de surface est légèrement atténué et en déphasage par rapport à celui du fond. Le système est nettement plus turbulent en avril-mai.

where P is the partial pressure of CO_2 in the water column, and Σ is the total CO_2 species concentration. β varies with pH as best shown by the following set of equations giving the variations of total carbonate, total bicarbonate, total dissolved CO_2 and carbonate alkalinity as a function of pH:

$$\partial c/\partial H = [K_2 (H+2 K_2)(\partial A/\partial H) - K_2 A]/(H+2 K_2)^2, \quad (1)$$

$$\partial b/\partial H = [H (H+2 K_2)(\partial A/\partial H) + 2 K_2 A]/(H+2 K_2)^2 \quad (2)$$

$$\partial s/\partial H = [AH/K_1 (H+2 K_2)] + [(H/K_1)(\partial b/\partial H)] \quad (3)$$

and, since total alkalinity TA is constant,

$$\partial A/\partial H = -\partial B^-/\partial H - \partial OH^-/\partial H + 1$$
$$= K_B B_T/(H+K_B)^2 + K_W/H^2 + 1 \quad (4)$$

with

$c = [CO_3^{2-}]$,
$b = [HCO_3^-]$,
$s = [CO_2] + [H_2CO_3] = [CO_2]_{(s)}$,
$B^- = [B(OH)_4^-]$,
B_T = total borates (Culkin, 1975),
$H = [H^+]$,

Table 1

Extreme values of pH in seawater in September 1981 and April-May 1982; corresponding speciations of CO_2 and borate.

Valeurs extrêmes du pH de l'eau de mer en septembre 1981 et en avril-mai 1982; spéciations correspondantes du CO_2 et du borate.

	September - 8 m TA = 2.60 T° = 22.5°C S°/oo = 38.0				September - Surface TA = 2.60 T° = 24°C S°/oo = 38.0		
	pH min	pH max	Δ		pH min	pH max	Δ
	8.037	8.084	+0.047		7.965	7.993	+0.028
B	0.084	0.092	+0.008	B	0.075	0.079	+0.004
A	2.516	2.508	−0.008	A	2.525	2.521	−0.004
b	2.152	2.111	−0.041	*b*	2.197	2.175	−0.022
c	0.182	0.199	+0.017	*c*	0.164	0.173	+0.009
s	0.020	0.017	−0.003	*s*	0.023	0.022	−0.001
Σ	2.354	2.327	−0.027	Σ	2.384	2.369	−0.015
P	644	567	−77	P	794	736	−58

	April-May - 8 m TA = 2.58 T° = 13.2°C S°/oo = 38.0				April-May - Surface TA = 2.58 T° = 14°C S°/oo = 38.0		
	pH min	pH max	Δ		pH min	pH max	Δ
	8,146	8.190	+0.044		8.139	8.177	+0.038
B	0.090	0.098	+0.008	B	0.090	0.097	+0.007
A	2.490	2.482	−0.008	A	2.490	2.483	−0.007
b	2.141	2.103	−0.038	*b*	2.138	2.105	−0.033
c	0.175	0.190	+0.015	*c*	0.176	0.189	+0.013
s	0.017	0.015	−0.002	*s*	0.017	0.016	−0.001
Σ	2.333	2.308	−0.025	Σ	2.332	2.310	−0.022
P	436	387	−49	P	448	404	−44

Conc. in millimoles l^{-1} seawater.
Partial pressure in ppm.

Conc. en eau de mer (millimoles l^{-1}).
Pression partielle en ppm.

$B = [B(OH)_4^-]$; A = carbonate alkalinity = $b + 2c$; $b = [HCO_3^-]$; $c = [CO_3^=]$; $s = [CO_2]_{(s)}$; Σ = total inorganic carbon = $s + b + c$; $P = PCO_2$ in seawater; TA = total alkalinity = $A + B$.

$B = [B(OH)_4^-]$; A = alcalinité carbonatée = $b + 2c$; $b = HCO_3^-]$; $c = [CO_3^=] >$ $s = [CO_2]_{(s)}$; Σ = carbone inorganique total = $s + b + c$; $P = PCO_2$ dans l'eau de mer; TA = alcalinité totale = A + B.

Remark: Gradients cannot be calculated from Table 1; they are evaluated using Figure 2 and similar curves, since the surface signal lags behind the bottom one.

Les gradients ne peuvent être calculés à partir de la table 1; ils sont calculés à partir des courbes telles que représentées sur la figure 2, car le signal de surface est retardé par rapport au signal de fond.

K_1, K_2 = carbonic acid constants (Mehrbach *et al.*, 1973; Millero, 1979),

K_B = boric acid constant (Lyman, 1957 cited by Millero, 1979 and by Hansson, 1973),

A = carbonate alkalinity (usually C.A.),

TA = total alkalinity = $A + B^- + [OH^-] - [H^+]$,

K_W = water dissociation constant (Hansson, 1972 cited by Millero, 1979),

$\partial/\partial H$ = partial derivatives.

By introducing (4) in (1), (2) and (3), one finds the expression of the homogenous buffer factor β:

$$\beta = (\partial P/P)/(\partial \Sigma/\Sigma)$$
$$= [1 + K_1K_2/H^2 + K_1/H]/[1 + (\partial b/\partial s) + (\partial c/\partial s)] \quad (5)$$

where

P = partial CO_2 pressure in seawater (usually PCO_2),

Σ = total inorganic carbon (usually ΣCO_2).

Another expression of the buffer factor is

$$\beta' = \partial\Sigma\, CO_2/\partial pH \qquad (6)$$

(*see* Riley, Skirrow, 1975, p. 11), as used in classical physical chemistry when dealing with weak acids and bases. In practice it is easily calculated from :

$$\beta' = -2.303\frac{\Sigma}{P}.10^{-pH}\left(\frac{\partial P}{\partial H}\right).\beta^{-1} \qquad (6')$$

with $\partial\Sigma/\partial H$ given by the sum of eq. (1), (2) and (3), $\partial\Sigma$ = equivalents of acids and bases added to seawater.

The buffer factor as defined above can be used as a measure of the effect on the carbonic acid system of adding or retrieving given amounts of dissolved CO_2, CO_3^{2-}, HCO_3^- (biological activity, air-sea exchanges). In the case of exchange of carbonate with a solid phase, the system of equations (1)-(5) is not valid since the variations of carbonate alkalinity do not then depend only on pH.

Sundquist *et al.* (1979) have used equations similar to (1)-(5) (constant total alkalinity system) to evaluate the extent to which the different sets of dissociation constants found in the literature lead to different estimations of β. We concentrate attention on the variations of the buffer factor with pH, but our results are in agreement with those of Sundquist, although slightly lower values (0.5 %) are obtained for β at pH > 8.2, due to the fact that we take into account the dissociation of water (*see* also Sundquist, Plummer, 1981).

Figure 3 gives β, the carbonate alkalinity, the carbonate concentrations and the terms $\partial c/\partial H$, $\partial b/\partial H$, $\partial s/\partial H$ as a function of pH for a constant total alkalinity system as observed in the Bay of Calvi (20°C, 38 ‰, CA = $2.600.10^{-3}$ eq.l^{-1} at pH 7.5 and TA = $2.630.10^{-3}$ eq.l^{-1} = constant). β is also given at 12°C.

The values for β calculated for the same seawater but with the hypothesis of the constant CA regime of Mac Intyre (1978), are also indicated in Figure 3*A*. When

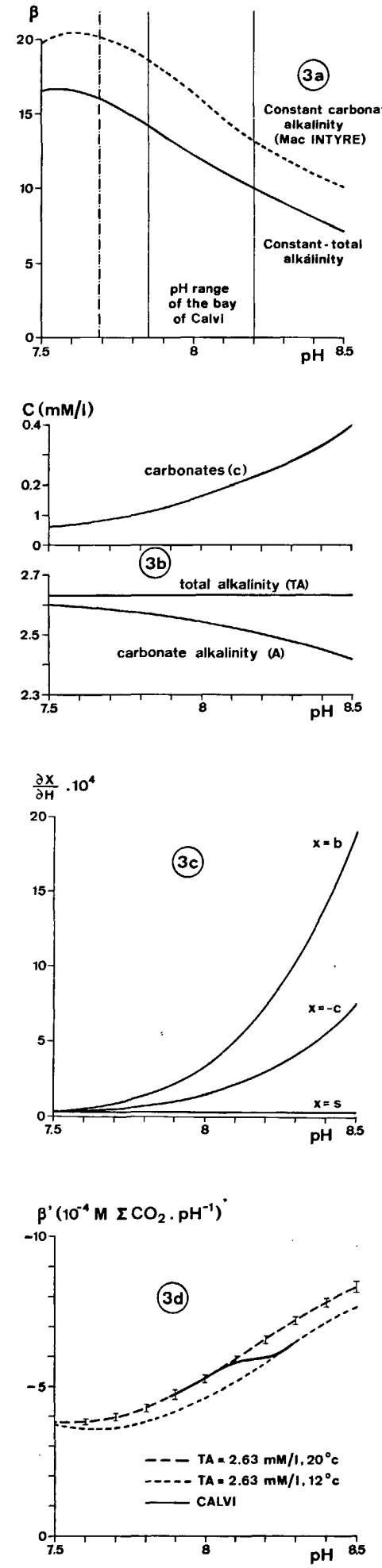

Figure 3

Theoretical buffer factor β *[equation (5)] for a constant-total alkalinity system and a constant-carbonate alkalinity system (dotted line: Fig.* 3 A) *calculated at* 20°*C and S* = 38 ‰. *Total alkalinity, carbonate alkalinity and carbonate concentration are shown in Figure* 3 B *(with A* = 2.600 *meq.l*$^{-1}$ *at pH* 7.5; *hence TA*= 2.630 *meq.l*$^{-1}$). *Figure* 3 C *shows* $\partial c/\partial H$, $\partial b/\partial H$ *and* $\partial s/\partial H$ *[eq.* (1), (2), (3)] *as a function of pH. Figure* 3 D *gives theoretical (broken lines) at* 20°*C and* 12°*C and experimental* β' *(continuous line) buffer factor* ($\partial\Sigma/\partial pH$) *corresponding to the* in situ *conditions. Vertical I show the effect of increasing TA from* 2.630 *meq l*$^{-1}$ *(chosen case) to* 2.650 *meq.l*$^{-1}$ *and* 2.600 *meq.l*$^{-1}$.

Pouvoir tampon théorique β calculé à 20°C et pour S = 38 ‰ [équation (5)] pour un système à alcalinité totale constante et un système à alcalinité carbonatée constante (ligne en pointillé, fig. 3 *A*). L'alcalinité totale, l'alcalinité carbonatée et la concentraiton en carbonate sont montrées dans la figure 3 *B* (avec A = 2.600 méq.l^{-1} à pH 7,5; donc TA = 2.630 méq.l^{-1}). La figure 3 *C* montre $\partial c/\partial H$, $\partial b/\partial H$ et $\partial s/\partial H$ [équations (1), (2), (3)] en fonction du pH. La figure 3 D donne les valeurs théoriques (lignes interrompues) à 20°C et 12°C et les valeurs expérimentales (lignes pleines) du pouvoir tampon β' ($\partial\Sigma/\partial pH$) correspondant aux conditions *in situ*. Les I verticales montrent l'effet d'une variation d'alcalinité totale de 2.630 méq.l^{-1} (cas choisi) à 2.650 méq.l^{-1} et 2.600 méq.l^{-1}.

Table 2
Calculated in situ β *and corresponding measured mean pH and temperature.*
β calculé *in situ* et valeurs correspondantes du pH moyen mesuré et de la température.

	Mean pH	T° (C°)	β
May 80	8.20	12.8	11.02
June 80	8.09	18.8	11.33
July 80	8.06	19.8	11.57
August 80	7.92	22.2	12.99
October 80	8.02	20.8	11.81
May 81	8.16	15.5	10.99
June 81	8.08	19.5	11.37
July 81	8.05	21.5	11.43
September 81	8.06	22.5	11.08
December 81	8.20	11.8	11.08
March 82	8.25	11.8	10.45
April 82	8.17	13.2	11.20

borates are taken into account, the maximum of β is displaced towards a more acid pH. The absolute value is smaller, as expected: the borates increase the capacity of seawater to absorb, for instance, CO_2 in excess in the atmosphere. Figure 3 *C* provides evidence that the decrease of β at pH > 8 (which means increased buffer capacity) is due to the variations of carbonate and bicarbonate concentrations which for a given ΔpH or ΔH become more and more important compared to dissolved $CO_{2(s)}$. The $\partial s/\partial H$ decrease when pH increases is negligible in the chosen pH range.

It should further be noted that $\partial b/\partial c$ is characteristic of the chosen system, either at constant carbonate alkalinity or at constant total alkalinity. For the former $\partial b/\partial c = -2$. For the latter $\partial b/\partial c$ depends on A and on $\partial A/\partial H$ [equations (2), (3) and (4)]. Under the conditions found in the Bay of Calvi, $\partial b/\partial c$ is close to -2.46.

Table 2 gives β values calculated from the data collected during several campaigns from May 1980 to April 1982. The extremes are 13 and 10.5 and the state of the system is moving between these two values.

Similarly, Figure 3 *D* represents $\beta' = \partial\Sigma\ CO_2/\partial pH$ [*see* eq. (6) and (6′) at 20°C and 12°C with again TA = 2.63. The continuous line corresponds to the in situ values of β′ calculated using observed temperature, mean pH and TA values. β′ as does β moves from the theoretical curve at 20°C to reach the one at 12°C during the year. The effect of the absolute value of TA is small in the range 2.60-2.65 as shown by the size of the vertical bars on the 20°C curve (β′ increases with increasing TA).

The transition described by MacIntyre (1978) towards the constant carbonate regime where the carbonate concentration is kinetically maintained by dissolution of solid carbonates, is not reached and the constant total alkalinity regime describes very well the CO_2 system in the pH range 7.83-8.25, as shown by the two full vertical lines in Fig. 3 *A*. The vertical broken line indicates when the carbonates start to dissolve (pH > 7.7) using the apparent solubility constant for aragonite as given by Edmond and Gieskes (1970) (Riley, Skirrow, 1975). The solubility ratio of aragonite/calcite is 1.3 (Morse *et al.*, 1980; Wollast *et al.*, 1980), the concentration ratio is about 4. One should however bear in mind that if, at a macro scale, the water of the Bay of Calvi (which is typical of the Mediterranean water) does not actually reach the constant carbonate regime, it might do so at a micro scale (dead leaf material or inside, in sediment pore water), when the pH can become sufficiently low.

Figure 4 shows annual variations of the height of pH, $\Sigma\ CO_2$ and dissolved CO_2 diel signals observed in the 8 m water column above the seagrass bed. The variations are maximal from May to July and drop to zero in December. This corresponds very well to the evolution of the biological activity of the seagrass bed which becomes senescent from midsummer on (Bay, 1978). New leaves are produced progressively from September to August of the next year, growth culminating in July.

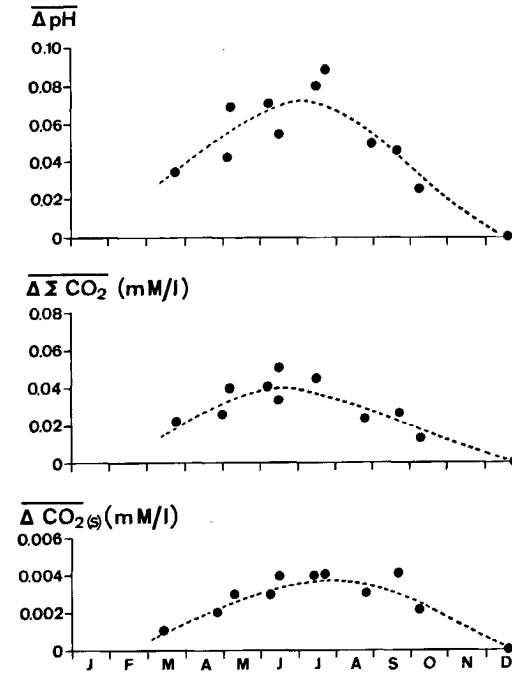

Figure 4
Values of diel in situ *observed pH changes and corresponding calculated values of diel change of* $\Sigma\ CO_2$ *and dissolved* $CO_{2(s)}$ *(TA is constant).*
Valeurs du signal journalier de pH observé *in situ* et valeurs calculées correspondantes de $\Sigma\ CO_2$ et de CO_2 dissous (TA constante).

The photosynthetic activity of the Posidonia bed varies, of course, as a function of temperature and luminosity: $Q_{10} \simeq 2\text{-}3$ (Bay, 1978; *see* also Vidaver, 1972); maximum temperature: 22°C, minimum: 12°C; maximum incoming solar radiation: 600 ly d^{-1}, minimum: 80 ly d^{-1} (ly d^{-1}: langlies per day).

Figure 5 describes the annual variations of measured total alkalinity (TA), of the mean pH at —8 m recorded during 2 or 3 days, of the calculated mean value of $\Sigma\ CO_2$, as well as of the mean PCO_2 in seawater. The maximum acidity observed during summer coïncides with the maximum amplitude of the diel pH change and corresponds to a maximum of dissolved CO_2 concentration (e.g. to a maximum of CO_2 partial pressure), a minimum and maximum for the carbonate and bicarbonate concentrations respectively. Nearly 45% of the maximum acidity in summer is explained by the

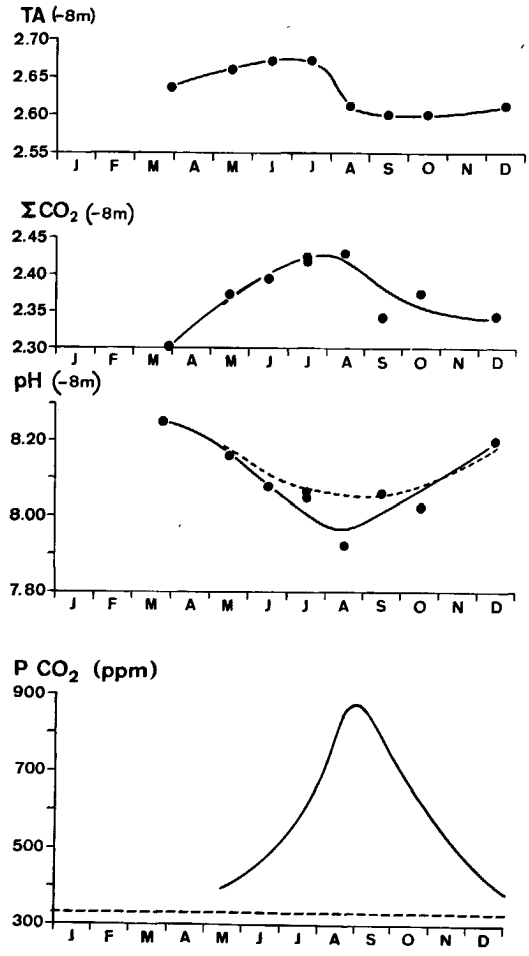

Figure 5

From top to bottom: — annual observed variation of total alkalinity (TA) in meq.l^{-1}; – annual calculated variation of mean ΣCO_2 in mM l^{-1} (−8 m); – annual observed variation of mean pH at −8 m; (– –) calculated variation of pH at constant TA, taking into account the theoretical temperature dependence of pH (starting with pH = 8.2 at 12°C); – annual calculated variation of mean PCO_2 in the water column. (– –) observed atmospheric partial CO_2 pressure.

De haut en bas : – variation annuelle mesurée de l'alcalinité totale (TA) en méq.l^{-1}; – valeur moyenne de ΣCO_2 calculée en mM l^{-1} à −8 cm; — variation annuelle mesurée du pH moyen à −8 m; (——) variation de ph calculée à alcalinité totale constante, montrant l'effet de la température, partant de pH=8,2 à 12°C; — variation annuelle calculée de PCO_2 moyenne dans la colonne d'eau (– –) pression partielle atmosphérique de CO_2 mesurée.

effect of temperature (the temperature dependency of the dissociation constants of weak acids induces a $\Delta pH/\Delta T$ = —0,012 UPH/C°) and it can be easily calculated that another 45% correspond to the change in total alkalinity [equation (4)].

It is obvious from Figure 5 that if TA can be taken to remain constant for a small time interval (several days), this assumption is not valid on a year basis. The significative drop of TA from July to August (ΔTA = 0.06 meq.l^{-1}, ΔCA = 0.04 meq.l^{-1}) is followed by a slow recovery lasting until July of the following year. The curve for CA, not given here, shows the same trend, but reduced.

According to Bay (1978), dried new leaf material contains 15% in weight of carbonate and 40% of acid resistant carbon, thus $CaCO_3$ corresponds to 35.9% in weight of total carbon. In June, the net photosynthesis of new leaves requires 5.3 g C m^{-2}d^{-1} (*see* further) and the carbonate-intake is 1.9 g $CaCO_3$ m^{-2}d^{-1}. The water column being 8 m deep, this corresponds to a decrease of TA equal to 0.14 meq.l^{-1} month^{-1}. The same approach applied to old leaves (which contain 50%) in weight of carbonate) gives a decrease of TA = 0.84 meq.l^{-1} month^{-1}.

This largely exceeds the observed annual change of TA shown in Figure 5, which reflects a balance between continuous $CaCO_3$ fixation and redissolution, enhanced by microenvironmental acid conditions, since Posidonia dead leaf debris only contains 20% of carbonate. The carbonate fixed in the leaves during 1/2 year or more would return to the water column during the senescent period.

Whatever the difficulties in explaining the observed TA changes in the water column, Figure 5 indicates that the system tends to reach an equilibrium between dissolution and removal of carbonates. The slow yearly increase compensates for the change between June and September. The kink between July and August must be caused by a sudden increase of fixation of carbonate which obviously cannot be related to the growth of Posidonia.

However, epiphytes such as Melobesiae grow very fast during that period (Mesureur, 1981) and produce an abrupt increase of 15% of the carbonate content of old leaves (Bay, 1978). This would result in a theoretical decrease of TA as calculated above. The fact that the calculated change is 4 times too high can be explained by the fact that all leaves do not bear equal amounts of epiphytes.

The possibility of chemical desaturation of the bulk water by carbonate precipitation because of the increased temperature during summer can be discarded. The degree of oversaturation for calcite is still around 300% (20°C) in summer (Fig. 6).

When dealing with time scales of a year, hydrodynamic features should not be overlooked: for instance, upwellings, increased mixing during winter and spring might slowly modify the quality of the water mass, leading to an increase of CA or TA which also depends on the residence time of the Bay. Further, the water above

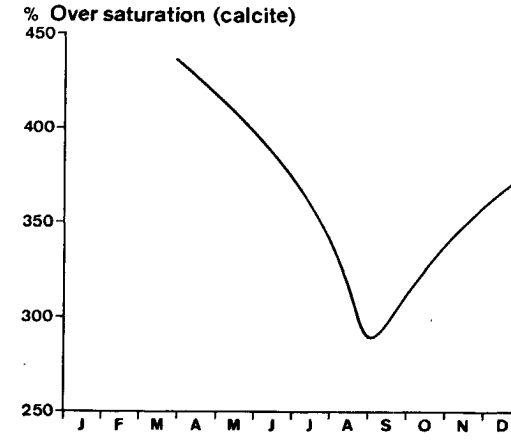

Figure 6

Annual variation of calculated percentage oversaturation of surface water for calcite.

Variation annuelle du pourcentage de sursaturation en calcite dans l'eau de surface.

the thermocline in which our measurements are made has obviously a different composition from that below, and the next step in the study we have undertaken will be to investigate the CO_2 system below and above the thermocline in deeper regions of the seagrass bed. To return to the question of maximum acidification in summer an increase of CO_2 in surface water during that period might also perhaps be expected because of an increased sewage input from the town of Calvi, where overcrowding is obvious in summer (3 500 inhabitants in winter, with a sharp increase to 30 000 starting in June, ending in September). An important heterotrophic activity is observed in the vicinity of the town, 5 miles away from our experimental field, and an increased settling of organic matter there and in other regions of the Bay is observed. A contribution, albeit small, to the overall detected increase of acidity, is theoretically to be expected, as well as an increase in dissolved carbonate. However, from preliminary data it may be shown that the seagrass bed can be mapped from pH transects; mixing with adjacent regions seems very small.

The yearly evolution of the carbonic acid system is obviously produced, as observed in all marine systems, by slow conflicting events which need to be clarified by further experiments and long temporal series.

The net photosynthetic activity of the seagrass bed can roughly be calculated from the ΣCO_2 change during day time and night and on a yearly basis by integrating the $\Delta\Sigma CO_2$ curve in Figure 4.

Bay (1978), monitoring O_2, states that the mean respiration rate of Posidonia is about 25% of the gross photosynthetic rate and that the same figure holds to evaluate the respiration rate of other sources (sediments including roots, bacteria, in-fauna, surface microflora and fauna, etc.). This would include, as far as CO_2 changes are concerned, the release of CO_2 by fixation of carbonate which can be neglected on a daily basis.

Using our results for $\Delta\Sigma CO_2$, we calculate (by integration of the diel signal over the 8 m water column) that the maximum net photosynthesis rate due to Posidoniae is 5.3 g C $m^{-2}d^{-1}$ ($\Delta\Sigma CO_2 =$ 0.055 mM l^{-1}, end June pH signal).

Experiments by Bay (1978) in June 1976 give 5.8 g C $m^{-2}d^{-1}$. The photosynthesis of phytoplankton in the water column above the seagrass bed represents on the average about 10% of the global effect. It has not been taken into account here, having been measured only occasionally.

A more rigorous treatment would require, in addition to *in situ* global $\Delta\Sigma CO_2$ and pH measurements, a compartmental analysis using transparent and dark half cylinders to isolate a seagrass tuft, a typical sediment surface, closed cylinders to measure respiration and photosynthesis in the water column. Dissolved and suspended organic matter has to be taken into account (*see* Johnson *et al.*, 1981). This analysis is in progress, and will be described in another paper.

Wehren *et al.* (1981) give in May 1981

$\Delta O_2 = 0.068$ mM l^{-1} (12 hours, direct measurement),

$\Delta CO_2 = 0.078$ mM l^{-1} (12 hours, calculated observed pH and TA).

The global RQ = 1.14, the PQ for Posidonia, assuming that the other sources of CO_2 have a rate equal to 25% of that of gross photosynthesis, is 1.16.

Integration of the $\Delta\Sigma CO_2$ yearly curve (Fig. 4) gives a net photosynthetic production of 696 g C $y^{-1}m^{-2}$ which corresponds fairly well with the 730 g C $y^{-1}m^{-2}$ given by Bay (1978).

Preliminary study of the air-sea exchange of CO_2

Using the floating bell method described earlier in this paper, we have attempted to correlate the observed CO_2 fluxes and the local physico-chemical variables determining release or capture of CO_2 by the sea. Theoretically, the flux depends on the difference of CO_2 partial pressure between air and sea, which is related to the temperature difference between the two phases, the CO_2 changes in the water column and in the atmosphere, the latter being very small in comparison with the former.

Figure 7 shows the annual variations of the temperature difference between sea and air and the mean measu-

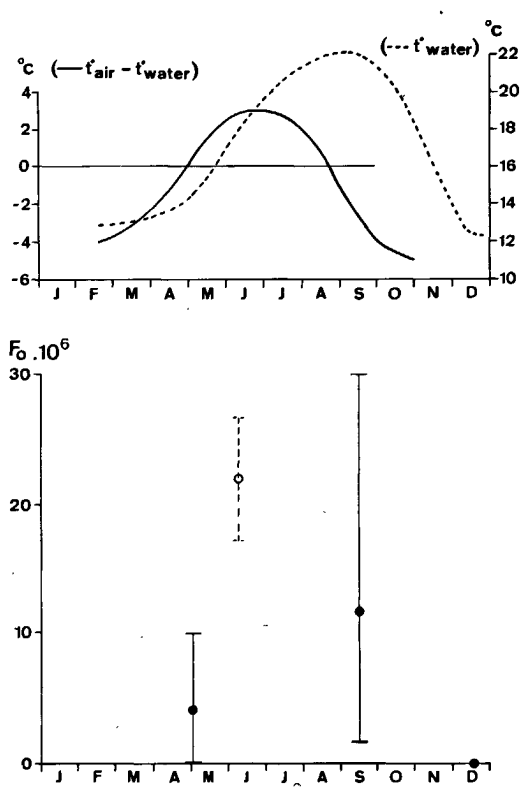

Figure 7

From top to bottom:

— t° air-t°water annual variation (annual variation of water temperature is shown in dotted line — right scale);

— CO_2 mean outfluxes in mg CO_2 $cm^{-2}min^{-1}$ (1 mg CO_2 $cm^{-2}min^{-1} = 3.79 . 10^{-3}$ Mol. CO_2 $m^{-2}sec^{-1}$; vertical bars indicate the dispersion of the observations).

De haut en bas :

— variation annuelle de la différence des températures de l'eau et de l'air (la variation annuelle de la température de l'eau est donnée en trait interrompu — échelle de droite);

— flux sortant mesuré de CO_2 en mg de CO_2 $cm^{-2}min^{-1}$ (1 mg CO_2 cm^{-2} $min^{-1} = 3,79 . 10^{-3}$ moles CO_2 m^{-2} sec.$^{-1}$).

red fluxes during 4 sampling periods. Fluxes were measured in May, June and September, with a maximum in June. In December no measurable flux can be detected. The summer maximum is clearly related to t°_{air}-t°_{water} which reaches a positive maximum leading to the degassing of the microlayer.

If the atmospheric partial pressure does not vary much during the year, the CO_2 partial pressure in water increases from 380 ppm in December to reach 950 ppm in August (maximal acidification) promoting the escape of CO_2 during summer (Fig. 5).

The CO_2 partial pressure in water is calculated from pH and alkalinity measurements. It could be determined directly, but the precision of our absolute pH measurements (0.01 pH unit) introduces a relative error on PCO_2 water of only 3%, which is of the order of magnitude of the precision of direct experimental measurements (chromatography, membrane electrodes). The relative error on the determination of PCO_2 air is also 3% (*see* material and methods, calibration of IR spectrophotometer).

The December situation is intriguing. No flux is measured, but the CO_2 partial pressure difference between the two phases is about 50 ppm and should theoretically result in an outflux. It appears that a significant overpressure is required to force the surface layer barrier which is kinetically controlled (hydration rate, surface film, properties, formation of bubbles).

From Table 2, we find in December $\beta = 11.1$ at mean pH 8.2, $t = 11.8°C$, PCO_2 water = 380 ppm. In March, $\beta = 10.45$, mean pH 8.23, $t = 11.8°C$, PCO_2 water = 360 ppm.

Fluxes have unfortunately not been measured in March, but must have been near zero or very small if account is taken of the December results (Fig. 5). It seems that the reentry of CO_2 in the sea might start at $\beta = 10$, that is pH 8.29, $t = 12°C$, PCO_2water = 300 ppm.

We also have looked at a possible correlation between outfluxes measured at hourly intervals, the physicochemical situation in the water column and the air partial pressure at sea level. Data are given in Figure 8 for a 48-hour cycle in May 1982.

The scattering of the flux measurements is considerable, although a maximum seems to be detectable around noon. This dispersion is most certainly related to experimentally uncontrollable events: sea state (waves, turbulence), degassing of O_2 (oversaturated during daylight) with bubbles entraining CO_2, etc. The air CO_2 partial pressure at 50 cm above sea level shows a small smooth change (air turbulence) with a maximum at midnight. One should, however, be careful in attempting to correlate these observations with the measured fluxes, since the situation in the air is probably also influenced by the nearby land: sparse bush vegetation is only a few hundred metres away.

The measured outfluxes and the calculated CO_2 partial pressure difference between sea and air permit determination of the so-called CO_2 evasion coefficients (Table 3, $k = F_0/\Delta PCO_2$) usually expressed in mmoles cm^{-2} min^{-1} atm^{-1}. The values are of the same order of magnitude as that quoted by Riley and Skirrow (1975), Smith and Atkinson (1983).

Table 3
Evasion coefficients measured in May 1982.
Coefficients d'évasion mesurés en mai 1982.

Hour	F_0	ΔP	k
12	$3.813.10^{-6}$	115	0.00075
14	$10.27\ .10^{-6}$	99	0.0024
16	$7.223.10^{-6}$	88	0.0019
18	$5.353.10^{-6}$	81	0.0015
20	–	69	–
22	$4.180.10^{-6}$	78	0.0012
24	$7.480.10^{-6}$	87	0.0020
2	–	98	–
4	–	103	–
6	$5.610.10^{-6}$	109	0.0012
8	0	105	–
10	$4.950.10^{-6}$	106	0.0011
12	$3.043\ 10^{-6}$	102	0.00068

Outfluxes (F_0) *in mg of* CO_2 $cm^{-2}min^{-1}$; ΔP *in ppm; k in mMoles of* CO_2 $cm^{-2}min^{-1}atm^{-1}$.
Flux sortants (F_0) en mg CO_2 $cm^{-2}min^{-1}$; ΔP en ppm; k en mMoles CO_2 $cm^{-2}min^{-1}atm^{-1}$.

We are aware of the fact that the methodology used to measure CO_2 fluxes *in situ* (initial escape velocity) inside a floating bell can be questioned: the bell might modify certain properties of the sea surface film, induces glass-house effects, and certainly affects air turbulence above the investigated surface.

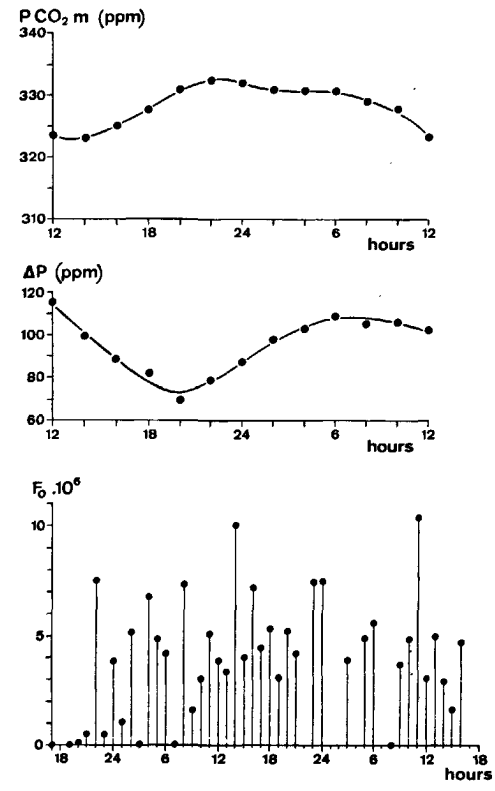

Figure 8
From top to bottom:
– diel change of observed partial CO_2 *pressure at 50 cm above sea level in May 1982;*
– diel change of $\Delta PCO_2 = PCO_2$ *water-*PCO_2 *air;*
– hourly observed outfluxes of CO_2 (F_0 *in mg* CO_2 cm^{-2} min^{-1}).
De haut en bas :
– variation journalière de la pression partielle en CO_2 mesurée à 50 cm au-dessus du niveau de la mer en mai 1982;
– variation journalière de $\Delta PCO_2 = PCO_2$ air;
– mesure horaire du flux sortant de CO_2 (en mg de CO_2 $cm^{-2}min^{-1}$).

Laboratory simulation experiments are in hand, with the aim of obtaining better knowledge of events controlled by the interface.

CONCLUSIONS

Mediterranean seagrass beds (that of the Bay of Calvi in Corsica being taken as an example) produce a very stable and reproducible diel CO_2, often almost sinusoïdal signal which is quickly transmitted through a 8 m homogenous seawater column.

The signal (photosynthesis-oxidative processes) rides on a slow annual variation of the physico-chemical variables, *e.g.* pH, which define the state of the seawater system. It can be used to evaluate the net photosynthetic production in terms of changes of ΣCO_2 in the water column.

The constant total alkalinity chemical model of seawater can be applied during experiments lasting a few days, and permits calculation of an internal buffer factor, $\beta = \partial \ln PCO_2 / \partial \ln \Sigma CO_2$ and $\beta' = \partial \Sigma CO_2 / \partial pH$. β oscillates between 10.5 and 13 over one year and it is believed that reentry could be expected to start at the critical value $\beta = 10.0$ in Mediterranean waters similar to that found in the west coastal zone of Corsica.

The buffer factor can theoretically be applied to the two-phase system, provided equilibrium is reached between sea and air partial pressure. Field measurements show that such a situation is never reached. The observed system emits CO_2 constantly except during winter, when no influx or outflux have so far not been detected (although a CO_2 partial pressure difference between sea and air of about 50 ppm is found). The outfluxes, if any, are—as expected—very small compared to the ΣCO_2 changes in the water column. The latter, which are a measure of the global biogeochemical CO_2 flux, are 50 to 100 times greater.

The surface barrier, measured by PCO_2sea-PCO_2air when there is no flux cannot be explained, but is most certainly linked to molecular, diffusion at the interface (hydration problems), together with the properties of the surface film (oil, organic complexes, different water structure, exploding bubbles, etc.) (*see* also Riley, Skirrow, 1975).

One might say that with respect to CO_2, the sea practically ignores the atmosphere. The communication through the sea-air interface is irregular, although in the water column CO_2 changes are smooth and regular at the site where our experiments were carried out. In sea regions, where there is a reentry of CO_2, the influxes are probably as scattered. This irregularity may reflect the fluctuating properties of the sea surface microlayer, and the surface layer appears as a source of hazardous events despite the regularity of the seawater CO_2 signal above the seagrass bed.

It is obvious that if seagrass beds indeed contribute to the reoxygenation of the water masses and the entrapment of large amounts of CO_2 by photosynthesis, thereby playing an important role in controlling pH, this process cannot however entirely cope with the overall acidification observed during summer resulting from increased temperature, enhanced oxidative processes probably related to the destruction of large organic matter output from land and local marine production.

The Posidonia belt around the Mediterranean sea should be taken as a CO_2 emitter, except in winter when the seagrass ecosystem appears to be neither a sink nor a source.

The authors believe it is unlikely that certain regions of the belt unspoiled by urban and industrial sewage could behave as permanent atmospheric CO_2 sinks under hydrographic conditions very different from that of the bay studied here.

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