# Study of the transmission of the diurnal $CO_2$ concentration changes observed above a *Posidonia* seagrass bed: a method to determine the turbulent diffusion coefficient in an 8-m water column

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**Abstract**—A simple method is presented to calculate the $CO_2$ vertical turbulent diffusion coefficient in the upper layer above a *Posidonia* sea grass bed. The method relies on the measurement of the attenuation and phase shift of the diurnal $CO_2$ variation at different depths in the water column. The values of the turbulent diffusion coefficient fall in the upper range of values given in the literature for the mixed layer ($\approx 10^{-2}$ $m^2$ $s^{-1}$), which is consistent with the high-energy environment studied.

## INTRODUCTION

THE *POSIDONIA* seagrass bed of the Bay of Calvi (Corsica) is the site of an important and very reproducible $\Sigma CO_2$ (total inorganic carbon) diurnal variation which is often almost sinusoidal. The understanding of its transmission through the water column is of importance in the study of $CO_2$ air–sea exchanges undertaken in this environment (FRANKIGNOULLE and DISTECHE, 1984).

The attenuation and phase shift of the $CO_2$ variation in the water column as a function of depth should, in principle, make it possible to estimate the vertical diffusion coefficient.

The difficulty of calculating the turbulent diffusion coefficient ($K$) from such data results, however, from possible $CO_2$ changes in the water column itself (advection, sea–air $CO_2$ exchanges, pelagic activity . . .).

At the chosen experimental site these contributions can often be neglected and a simplified analogical model can be used.

## MATERIAL AND METHODS

*Instrumentation*

The calculation of $\Sigma CO_2$ is based on pH and total alkalinity measurements. The immersed pHmeters are equipped with a pressure-compensated electrochemical cell (DISTECHE, 1959, 1964). Its great stability—due to the negligible junction potential—as well as the low noise permit one to measure 0.001 pH unit variations with very good reproducibility. Calibration is by phosphate buffer titration. Total alkalinity is determined by the GRAN (1952) method with a precision of 0.2%.

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It has been checked that the set of dissociation constants used (MEHRBACH *et al.*, 1973), the pH calibration, and the alkalinity determinations form a coherent system by adding known amounts of $Na_2CO_3$ to a given seawater (FRANKIGNOULLE and DISTECHE, 1984).

To study the transmission through an 8-m water column of the diurnal $CO_2$ variations generated by the seagrass bed, we moored one pHmeter near the surface (−50 cm) and one on the bottom (−8 m), just above the Posidoniae layer (September 1981, May 1982 and June 1984 campaigns). Figure 1 shows one example of the measured pH signals in June 1984 [see also FRANKIGNOULLE and DISTECHE (1984)].

The same display was used in October 1984, but, in addition, vertical pH profiles were recorded every 3 h with the surface probe.

*Calculation of K*

The diffusing species is assumed to be $\Sigma CO_2$ (carbonate, bicarbonate and dissolved $CO_2$). The rate of chemical equilibrium is very fast for the $CO_2$ system compared to the characteristic time-scale of the phenomenon we observe, and it is not necessary to distinguish each $CO_2$ species in particular in our diffusion model: we take the diffusion coefficient to be the same for all chemical species.

The source and sink of $\Sigma CO_2$ is the bottom layer, that is that layer which contains the dense seagrass tufts, 50–60 cm high, with ribbon leaves in continuous pendulating movement because of surface-wave action. The bottom layer is well-mixed and homogeneous (no gradients except at the sediment interface).

The water column is well-mixed, and there is no detectable haline or total alkalinity stratification.

The method consists in equating the transmission of the $\Sigma CO_2$ variation generated in the bottom layer through the water column as the transmission of an electrical signal through a delay network with known transmission characteristics. The general theory is based on Laplace transforms and permits the treatment of any type of signal. HILL (1948, 1949) has used this method to study the transmission of heat through a muscle membrane. DISTECHE (1960) has shown that is can be used to interpret pH surface measurements on muscles, correcting for instrumental and diffusion-caused time lags.

If $y_o$ is the instantaneous variation of $\Sigma CO_2$ in a homogeneous bottom layer considered as an infinite plane source, $y$ the measured value of $\Sigma CO_2$ at time $t$ and distance $z = h$ from this source, then [see CRANK (1979)]:
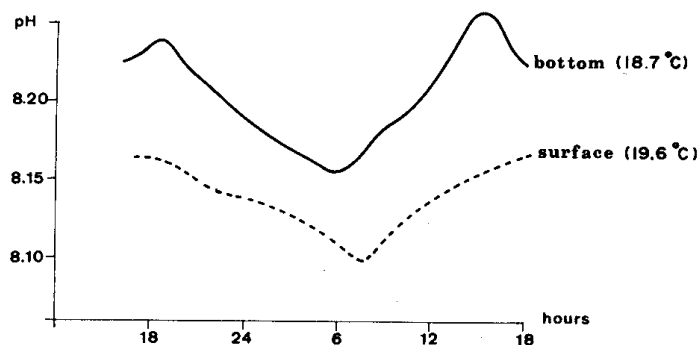


Fig. 1.   Typical pH variations recorded above the *Posidonia* seagrass bed in June 1984.

$$y/y_o = 1 - \mathrm{erf}\, h/(2Kt)^{1/2}, \tag{1}$$

where $K$ is the mean diffusion coefficient over time and depth.

If the source signal is subdivided into a series of discrete rectangular pulses of width $\theta$ and height $f_n$, corresponding to the observed $\Sigma CO_2$ concentration at time $\theta/2$, $3\theta/2$, $5\theta/2$, . . . $(n - \frac{1}{2})\theta$, then the corresponding signal height $(x_n)$ at distance $z = h$ from the bottom, at time $\theta$, $2\theta$, $3\theta$, . . . $n\theta$, can be calculated from:

$$x_n = \frac{1}{a_1}\,(f_n - a_2 x_{n-1} - a_3 x_{n-2} - \ldots - a_n x_1)\ \text{at time } n\theta, \tag{2}$$

where $f_n$ = mean signal value over the time interval on the bottom, $x_n$ = signal value at time $n\theta$ and distance $z = h$ from the bottom, and $a_n$ = coefficient that defines the transmission of an unitary rectangular concentration step [$y_o = 1$ in equation (1)] of infinite duration and calculated from:

$$1 = a_1 y_1 \text{ at time } \theta, \tag{3}$$

$$1 = a_1 y_2 + a_2 y_1 \text{ at time } 2\theta, \tag{4}$$

$$1 = a_1 y_n + a_2 y_{n-1} + a_3 y_{n-2} + \ldots a_n y_1 \text{ at time } n\theta. \tag{5}$$

In fact, the coefficients $a_n$ define the 'memory' of the system since they are used to calculate the value of $x_n$ at time $n\theta$ by taking into account the preceding values of $x$ at time $(n - 1)\theta$, $(n - 2)\theta$ . . . [see equation (2)]. One must choose a number $(i)$ of coefficients $(a)$ so that the effect of the value of $x$ at time $(n - i - 1)\theta$ on the value of $x$ at time $n\theta$ can be neglected.

Equation (2) becomes:

$$x_n = \frac{1}{a_1}\,(f_n - a_2 x_{n-1} - a_3 x_{n-1} - \ldots - a_i x_{n-i})\ \text{at time } n\theta. \tag{6}$$

Figure 2 shows the theoretical transmission of a unitary $CO_2$ step of infinite duration as a function of time with fixed $h$ (8 m) for different values of the turbulent diffusion
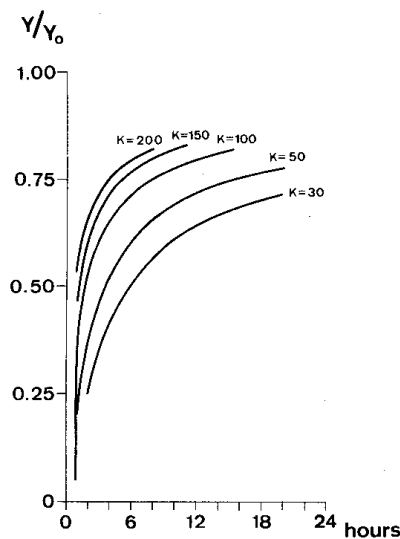


Fig. 2. Transmission through the 8-m water column of a unitary $CO_2$ pulse with infinite landing time for several values of the vertical turbulent diffusion coefficient $(K)$ (in $\times 10^4\ \mathrm{m^2\ s^{-1}}$).

coefficient. For $K = 0.02$ m$^2$ s$^{-1}$, 75% of the step variation has been transmitted 8 m above after 4 h against 16 h in the case of $K = 0.005$ m$^2$ s$^{-1}$. To each of these curves corresponds a set of coefficents $(a_1 \ldots a_n)$.

In practice, the observed bottom $\Sigma CO_2$ daily variation is approximated by a succession of hourly pulses of height equal to the value of the $\Sigma CO_2$ concentration at $\frac{1}{2}$, $\frac{3}{2}$, . . . $(n - \frac{1}{2})$ h; the surface signal is then calculated at $1, 2, \ldots n$ h for arbitrarily chosen mean values of $K$. The $\Sigma CO_2$ variations calculated at the surface are compared to the observed one. The best fit gives the $K$ value looked for. Trial and error show that $i$ in equation (6) can safely be limited to 12.

Since we deal with the transmission of a repetitive signal the calculations are carried out during three successive identical daily cycles to eliminate the obvious perturbations at the start of the first cycle.

The method can also be used to calculate the bottom variation from the surface one, that is to correct the time lag and attenuation introduced by diffusion.

## RESULTS AND DISCUSSION

We have applied the method described above to field measurements obtained in September 1981, May 1982, and June and October 1984. The results are summarized in Table 1. The choice of the coefficient $K$ which gives the best fit with the observations is based primarily on the comparison of the calculated and measured values of the maximal height $(X_s)$, and of the phase shifts at the maximum and minimum ($\Phi$) of the curves, and secondly of the detailed shape of the calculated surface $\Sigma CO_2$ variation (see Fig. 3). Table 1 shows that the best fit is obtained with $K = 0.0060$ m$^2$ s$^{-1}$ in September 1981, $K = 0.0160$ m$^2$ s$^{-1}$ in May 1982, $K = 0.0080$ m$^2$ s$^{-1}$ in June 1984, and $K = 0.0070$ m$^2$ s$^{-1}$ in October 1984.

The $(X_s)$ of the surface signal seems to be the best parameter to look at in order to choose the $K$ value since $X_s$ strongly depends on the value of the diffusion coefficient within the range calculated here (see Fig. 4). The error in the measured $\Sigma CO_2$ variation
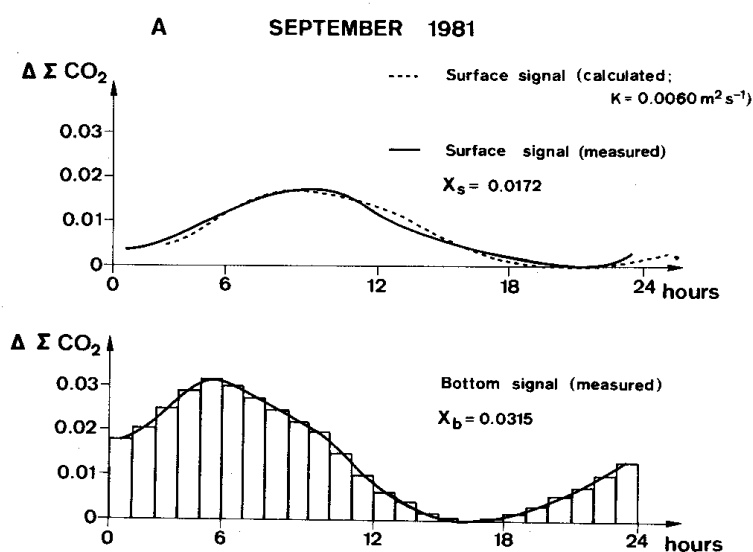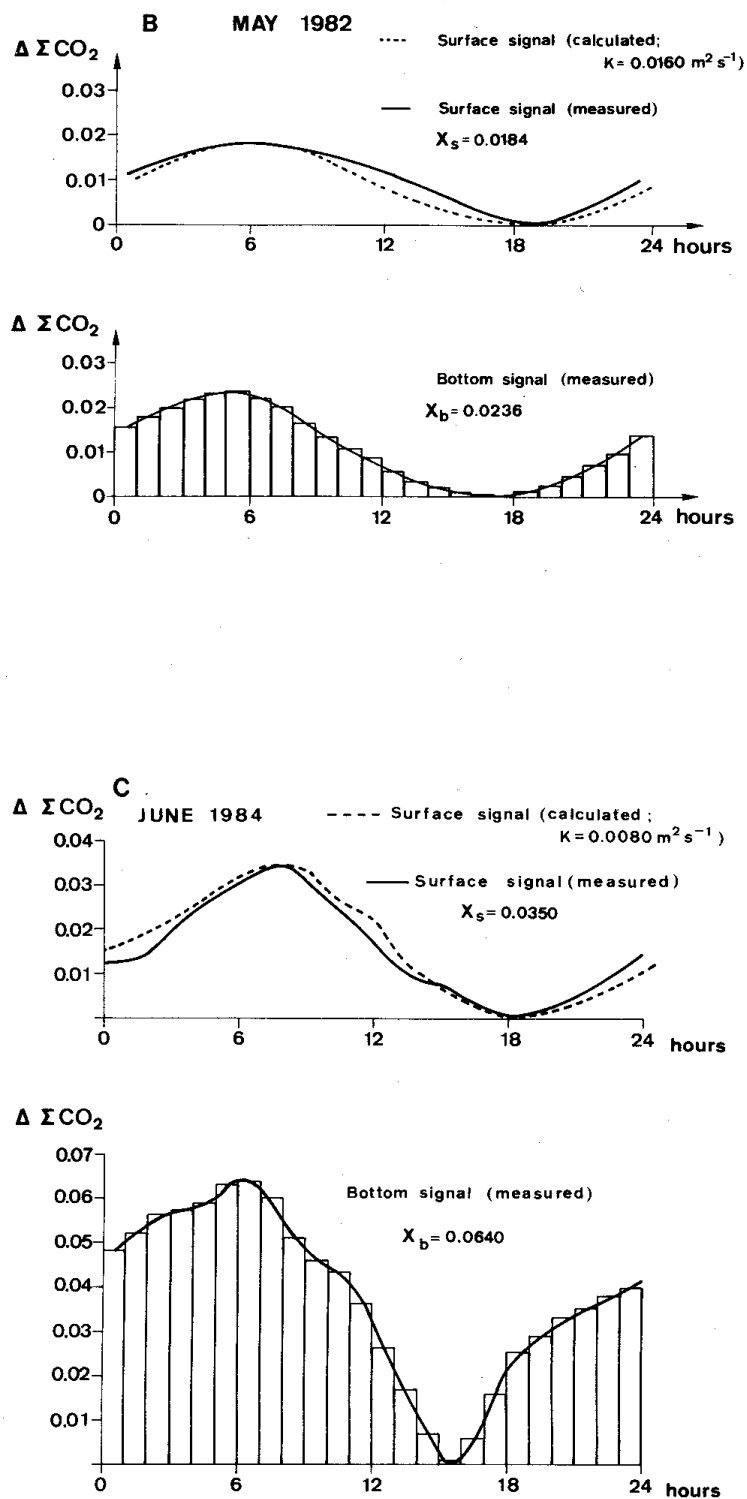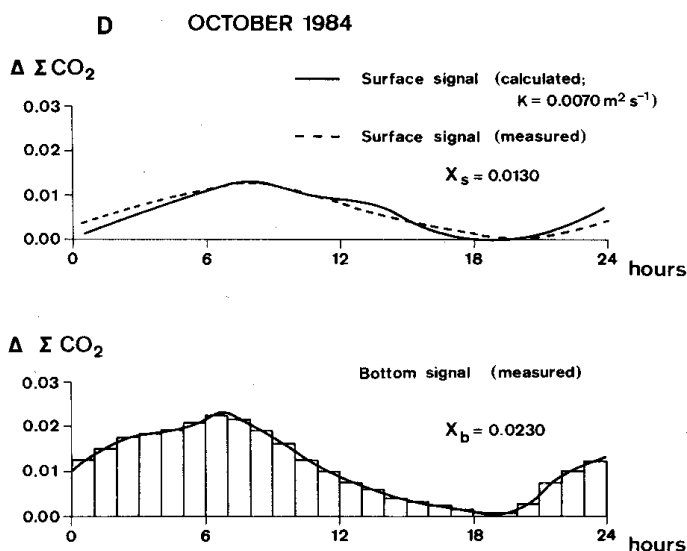


Fig. 3A.

Figs 3B,C.

Fig. 3.   Splitting of the bottom $\Sigma CO_2$ signal into hourly pulses: measured and calculated surface signals in September 1981 (A), May 1982 (B), June 1984 (C), and October 1984 (D). ($X$ = height, $\Delta\Sigma CO_2$ expressed in mM l$^{-1}$).

Table 1.   Values of the observed surface phase shifts ($\Phi_M$ = phase shift at the maximum height, $\Phi_m$ = phase shift at the minimum height, $X_b$ = maximal height on the bottom, $X_s$ at the surface) of the $\Sigma CO_2$ signal, calculated for different vertical turbulent mean diffusion coefficients K. $\Phi$ in s, $\Delta\Sigma CO_2$ concentrations in mM l$^{-1}$ [$\Delta\Sigma CO_2$ = 0 at the minimum (see Fig. 3)], K in m$^2$ s$^{-1}$

| September 1981 | | |
|---|---|---|
| Observed: $\Phi_M$ = 12,000, $\Phi_m$ = 14,000, $X_b$ = 0.0314, $X_s$ = 0.0160 | | |
| $K$ chosen | 0.0040 | 0.0060 | 0.0080 |
| $\Phi_M$ calc. | 13,500 | 12,000 | 7000 |
| $\Phi_m$ calc. | 14,000 | 13,000 | 8000 |
| $X_s$ calc. | 0.0112 | 0.0162 | 0.0178 |

| May 1982 | | |
|---|---|---|
| Observed: $\Phi_M$ = 3600, $\Phi_m$ = 5500, $X_b$ = 0.0236, $X_s$ = 0.0180 | | |
| $K$ chosen | 0.0140 | 0.0160 | 0.0180 |
| $\Phi_M$ calc. | 4500 | 3500 | 3000 |
| $\Phi_m$ calc. | 5000 | 5000 | 4500 |
| $X_s$ calc. | 0.0178 | 0.0180 | 0.0186 |

| June 1984 | | |
|---|---|---|
| Observed: $\Phi_M$ = 4800, $\Phi_m$ = 7500, $X_b$ = 0.0640, $X_s$ = 0.0350 | | |
| $K$ chosen | 0.0060 | 0.0080 | 0.0100 |
| $\Phi_M$ calc. | 5000 | 4500 | 4000 |
| $\Phi_m$ calc. | 9000 | 7000 | 4000 |
| $X_s$ calc. | 0.0302 | 0.0348 | 0.0362 |

| October 1984 | | |
|---|---|---|
| Observed: $\Phi_M$ = 3600, $\Phi_m$ = 3600, $X_b$ = 0.0230, $X_s$ = 0.0130 | | |
| $K$ chosen | 0.0050 | 0.0070 | 0.0090 |
| $\Phi_M$ calc. | 4500 | 3500 | 3000 |
| $\Phi_m$ calc. | 5000 | 4500 | 4000 |
| $X_s$ calc. | 0.0116 | 0.0126 | 0.0140 |

is small. It depends essentially on the error in the pH variation measurement (0.001 pH). In our "*in situ*" conditions pH $\simeq$ 8.1, total alkalinity $\simeq$2.6 meq $l^{-1}$, $t^o$ = 15–25°C, and $S$‰ = 38.0 [see FRANKIGNOULLE and DISTECHE (1984)], a variation of 0.001 pH induces a change in $\Sigma CO_2$ of $\leq$1 µm. Figure 4 shows that for $K$ = 0.0160 $m^2$ $s^{-1}$ this corresponds to an error of 0.0010 $m^{-2}$ $s^{-1}$ in $K$.

The surface phase shifts seem to be somewhat more difficult to reproduce (Table 1). The maximum offset found between calculated and measured values is equal to 18 min in September 1981 and October 1984 (phase shifts minimum). In fact, this offset is small in comparison with the difficulty in locating the maximum and minimum of the experimental curves (Fig. 3A), which may introduce an error of about 30 min in some cases.

Figures 3A–D show the measured bottom signals approximated by a series of rectangular pulses, the measured surface signals, and the calculated surface signals for the best $K$ values chosen from Table 1. It is obvious that the calculated surface signals take into account most of the irregularities in the bottom signals, but there are slight contour differences, although maxima and minima are very well represented; for example, the calculated level of $\Sigma CO_2$ is down 4 µM $l^{-1}$ at 1 h in May, and in excess of 5 µM $l^{-1}$ at 12 h and down to 5 µM $l^{-1}$ at 24 h in June. As explained, such differences can not be due to an error in the $\Sigma CO_2$ determination. The best explanation seems to admit that they are due to the limitation introduced by the choice of a constant mean value of the diffusion coefficient. Figure 4, as indicated above, shows the dependency of the height of the transmitted signal on the diffusion coefficient.

The contour differences observed in Fig. 3 could easily be explained by a variation of $K$ over time and or depth. Halving or doubling $K$ in the range 0.0150 $m^2$ $s^{-1}$ produces signal height changes of about 2–3 µm $CO_2$, which is of the order of magnitude of the contour differences we are dealing with.

The proposed values of $K$ fall in the upper range of those given in the literature in the mixed layer [PARKER, 1982; JAMART *et al.*, 1977; NIHOUL, 1974 (cited by PICHOT, 1980)] (about $10^{-2}$ $m^2$ $s^{-1}$). These rather high values (especially in May 1982) are, we believe, due to the fact that our measurements are carried out near the coast (about 10 m away from it), at a shallow depth (8 m) in a region where waves break on vertical irregular rocky out-crops, that is, in a high-energy environment.
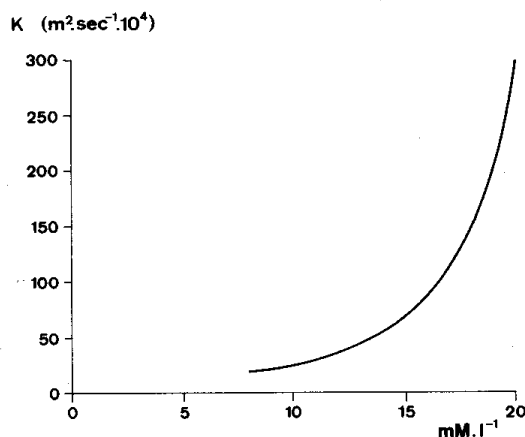


Fig. 4. Calculated maximal heights ($X_s$) of the surface $CO_2$ variation as a function of the diffusion coefficient $K$ (in $m^2$ $s^{-1}$) ($X_s$ in mM $l^{-1}$).

The high values of the diffusion coefficient in this case study are further confirmed by an analysis of $\Sigma CO_2$ profiles made at 3-h intervals in October 1984. Bottom and surface variations were recorded as usual.

Figure 5A shows the result of these experiments, Fig. 5B the calculated profiles applying the method described above at $z = 1, 2, 3, \ldots 8$ m to the bottom data for $K = 0.0070$ m$^2$ s$^{-1}$ (see Table 1); Fig. 5C, which corresponds to $K = 0.0020$ m$^2$ s$^{-1}$, is given for comparison; Figs 5B and C illustrate nicely how the theoretical gradients decrease and become practically constant when $K$ increases. The calculated gradients reverse sign around 10 and 21 h. Comparison of Figs 5A and B shows that the calculated profiles are in good agreement with the observed ones for $K = 0.0070$ m$^2$ s$^{-1}$. The gradient sign reversal predicted at 9 h happens between 10 and 11 h, and theoretical and observed reversals coincide at 21 h. It can be seen in Fig. 3$D$ that from 9 to 15 h the measured $\Sigma CO_2$ level is a little higher than the calculated one. As discussed above, this is probably due to a transitory increase in the diffusion coefficient which would in turn produce a sign reversal somewhat earlier than expected.

We will now examine approximations made by ignoring air–sea exchanges, sinks or sources of $CO_2$ in the water column, and advection.
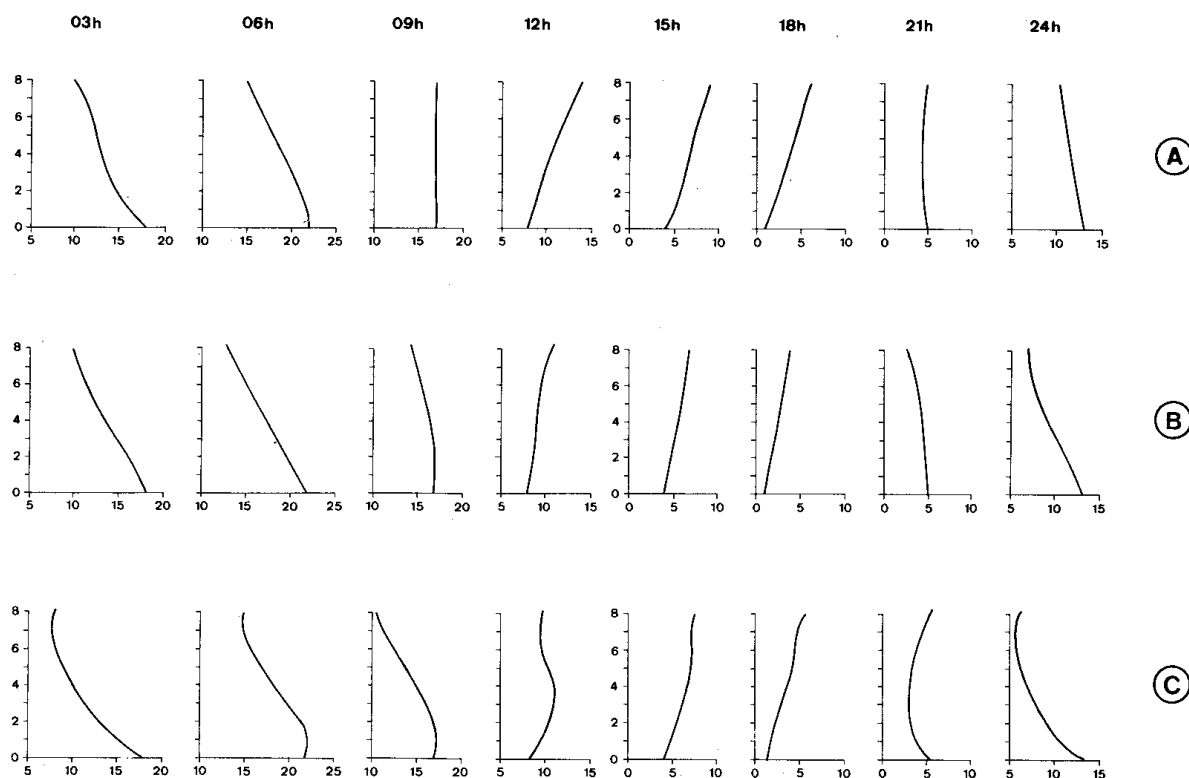


Fig. 5. Vertical $\Sigma CO_2$ profiles measured in October 1984 (A); and calculated from the bottom data with $K = 0.0070$ m$^2$ s$^{-1}$ (B), and $K = 0.0020$ m$^2$ s$^{-1}$ (C). Ordinate: distance from the bottom in m. Abscissa: $\Sigma CO_2$ level in $\mu$m l$^{-1}$ with $\Delta\Sigma CO_2 = 0$ at the minimum of the $\Sigma CO_2$ variation on the bottom. Note: the calculated profiles take into account the bottom data $\frac{1}{2}$ h sooner than the experimental ones because of the hourly-pulse approximation.

We have neglected air–sea $CO_2$ exchanges, since the measured $CO_2$ fluxes at the air–sea interface at this site are of the order of $10^{-7}$ M s$^{-1}$ m$^{-2}$ (FRANKIGNOULLE and DISTECHE, 1984), which corresponds to a variation of 1 µm l$^{-1}$ $\Sigma CO_2$ day$^{-1}$ in the 8-m water column.

A phytoplankton pelagic activity synchronous or not with the seagrass bed metabolism might blur the phase shift, since it occurs nearer to the surface: it would increase the amplitude of the surface signal, and the calculated $K$ would have a too large value. Fauna activity (fishes and zooplankton) would have little influence on both factors, corresponding to a more or less continuous release of $CO_2$ (respiration), very small compared to the fluctuating $CO_2$ signal from the *Posidoniae*. Field measurements show that both phyto- and zooplankton activites are maximal in the mixed layer of the Bay of Calvi during March and the begining of April (HECQ *et al.*, 1982). During this period, on some occasions the observed amplitude of the $\Sigma CO_2$ signals is in fact somewhat greater near the surface than on the bottom ($X_b$ = 0.022 mM l$^{-1}$, and $X_s$ = 0.025 mM l$^{-1}$ in March 1982). In this case, the determination of the diffusion coefficient is simply impossible with our simplified model. In May and September, however, the phytoplankton activity can safely be neglected as shown by results obtained in closed incubators located in the 8-m water column (FRANKIGNOULLE *et al.*, 1985).

Advection has also been neglected in the present analysis as, during calm weather (mean wind <5 m s$^{-1}$, occasional bursts of 10 m s$^{-1}$), when most of the experiments were carried out, the circulation in the Bay of Calvi is sluggish (<5 cm s$^{-1}$), and principally because it can be shown that horizontal pH gradients are very small [<0.001 pH units (100 m)$^{-1}$]. Moreover, the seagrass bed covers a very large surface [10 km$^2$ (BAY, 1978)] which determines the properties of the corresponding water layer of a given depth in contact with the seagrass bed.

Important advective processes bringing water layers of different chemical quality on the site of our experiments would most probably upset the agreement between calculated and observed $CO_2$ gradients as found in the cases selected in this paper.

To conclude we believe that the method described here gives realistic $K$s characteristic of a near-shore high-energy environment.

Using 3-h profiles, bottom and surface continuous measurements, we hope in the future to be able to integrate the diffusion equation numerically, and to calculate $K$ as a function of depth and time.

Further experiments need to be carried out to measure the turbulent diffusion viscosity, and field work on a different and less shallow site will include the study of the effect of the thermocline on the transmission of the $\Sigma CO_2$ variations. The results presented here are part of a larger programme on the biogeochemistry of $CO_2$, including air–sea exchanges. A proper evaluation of the level of turbulence in the water column is essential in this context.

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