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Daily and Yearly Variations of Total Inorganic Carbon in a Productive Coastal Area

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Daily variations of total inorganic carbon, calculated from pH and total alkalinity measurements, have been monitored in the Bay of Calvi, above a *Posidonia* seagrass bed, during 24 campaigns over a 6-year period and covering the four seasons. The *Posidonia* and phytoplankton differ in their spatial distributions and seasonal activities. By making use of the way in which the observed parameters in both surface and bottom waters change as a function of time, (on both a daily and a seasonal basis) it is possible to distinguish the individual contribution of the two types of plant to the observed parameter changes.

The data are sufficiently numerous to allow the testing of the variability of the daily mean values from year to year. It has been shown that the pH changes smoothly from 8·25 in winter to 7·9 in summer and shows good seasonal reproducibility. About one half of the seasonal change is due to the temperature dependence of pH. Total alkalinity and, as a consequence, inorganic carbon are less reproducible but show summer maxima despite sinks constituted by both the seagrass bed and the atmosphere. Except on a daily scale, carbon changes in the water column are not induced by primary production.

The large range of *in situ* physico-chemical conditions makes the Bay of Calvi an ideal area for the study of processes related to the inorganic carbon cycle.

Introduction

A proper understanding of the oceanic carbon cycle is vital if the consequences of atmospheric CO_2 perturbation induced by human activity are to be fully understood. Phenomena related to the carbon cycle are numerous and often of unknown intensity. Thus, most oceanic areas are the sites of irregular inorganic carbon changes which are often difficult to interpret. The study of processes which depend on CO_2 content, e.g. air-sea CO_2 exchanges, requires conditions free from the occurrence of sudden, rándomed variations.

A previous study by Frankignoulle and Distèche (1984) has shown that, due to a *Posidonia* seagrass bed, the Bay of Calvi is the site of a regular daily change in the water column. This paper describes results obtained during 24 campaigns over a 6-year period and covering the four seasons. Daily CO_2 changes are discussed in term of primary

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production and the numerous collected data allows the seasonal reproducibility of the CO_2 system parameters to be checked.

Material and methods

The total inorganic carbon is determined using continuous and *in situ* measurements of pH and temperature and determinations of total alkalinity and salinity.

The pH is monitored with the probe conceived by Distèche (1959, 1962) to be used under pressure. The precision of the measurement is 0·01 pH unit and the stability of the electrochemical cell allows the detection of 0·001 pH unit variations. Calibration of the pH meter is made by titrating standard phosphate solutions (Na_3PO_4 + NaCl added to reach a salinity of 38·00‰, i.e. approximating to that of the surface Mediterranean sea) as explained by Frankignoulle and Distèche (1984).

The total alkalinity is determined by the well known Gran (1952) titration method. Results are corrected to take into account fluorides and sulfates, as suggested by Hansson and Jagner (1973). The accuracy, established using standard carbonate, is 0·2%.

The total inorganic carbon concentration is calculated as proposed by Millero (1979), using dissociation constants for carbonic and boric acids determined on the N.B.S. scale (Hansson, 1973; Lyman, 1957; Mehrbach *et al.*, 1973). To calculate the speciation of total inorganic carbon into carbonate, bicarbonate and dissolved CO_2 forms, the CO_2 seawater solubility coefficient proposed by Weiss (1974) has been used and the borate concentration is calculated using the ratio of total boric acid to salinity given by Culkin (1965).

Results and discussion

Results presented in this paper have been obtained at the oceanographic research station Stareso (University of Liège) in the Bay of Calvi (Corsica, France).

The Bay is occupied by a dense seagrass bed (*Posidonia oceanica (L) Delile*) which covers a surface of 10·71 km^2 (Bay, 1984), i.e. half of the surface of the Bay. The depth range is between 1 and 38 m and is, in fact, nearly completely occupied by the seagrass.

The chosen experiment site is about 10 m far Stareso, above the seagrass bed, and the water column is 8 m depth.

Daily variations

In order to study daily changes of the total inorganic carbon in the water column, two pH probes were employed. The first was set on a metallic support embedded in the bottom and the other fixed to a float maintained above the bottom support. Measurements were made during at least a 24 h cycle, so as to allow for diurnal surface and bottom variations.

Previous work by Wheren *et al.* (1981) and Frankignoulle and Distèche (1984) have shown that the Bay of Calvi is the site of a regular and reproducible diurnal pH variation in phase with photosynthesis and respiration processes. The period following sunrise is characterized by a maximum of acidity (minimum of pH) and that of sunset by a minimum of acidity. Since daily variations of temperature (maximum 0·5 °C d^{-1}, summer), salinity (maximum 0·05‰ d^{-1}) and, more especially, of total alkalinity (maximum 2–4 μeq d^{-1}, see further) are always negligible, such pH variations as are noted are due to the input and output of dissolved CO_2. Figure 1 further provides supporting evidence that such

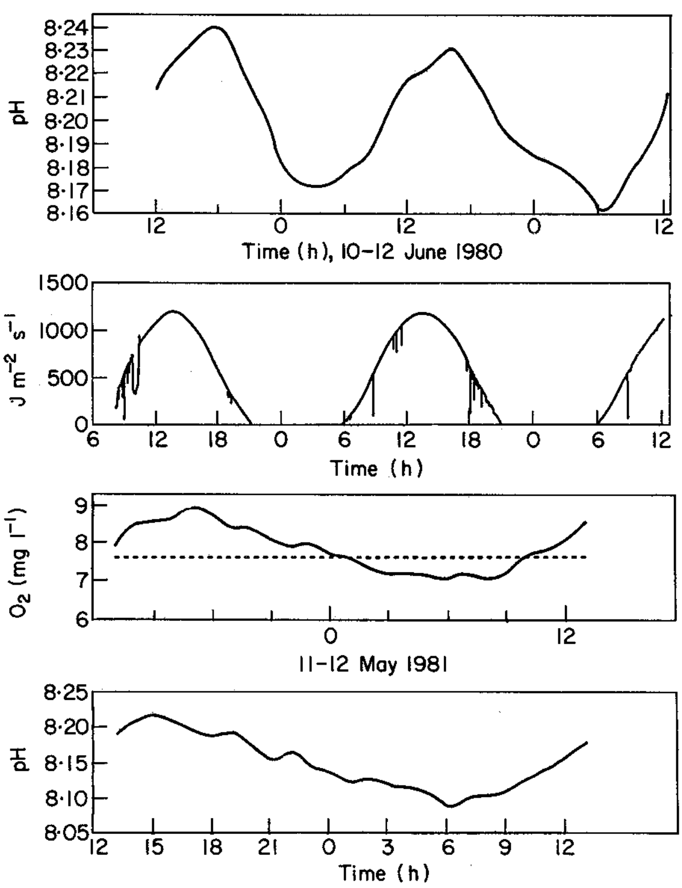

Figure 1. Daily pH variations monitored at 8 m depth in relation with incoming solar irradiance and dissolved oxygen.

variations agree well with those of dissolved oxygen and solar irradiance and imply that they arise from photosynthesis and respiration processes. That is, they result from the seagrass bed or from phytoplankton activity, or from both causes. However, since the seagrass bed and the phytoplankton have sufficiently different characteristics, on both spatial distribution and seasonal activity, it is possible to distinguish the individual contributions to the overall activity on the basis of their individual effects on inorganic carbon changes in the water column.

In the Bay of Calvi, the phytoplankton has a high maximum activity (the so-called ' bloom ') in early spring as a consequence of the increase of solar irradiance and of the high level of nutrients brought to the surface layer by winter mixing of water masses (Hecq *et al.*, 1982). The bloom is very brief, because the nutrient level is quickly reduced and, moreover, the herbivorous zooplankton consume much of the phytoplankton biomass. Since the phytoplankton is homogeneously distributed in a coastal 8 m water column, surface and bottom variations of inorganic carbon arising from phytoplankton activity should be similar.

On the other hand, the activity of the *Posidonia* seagrass bed is independent of the nutrients' level in the water column, and the annual course of its activity is more regular since it is essentially a function of the incoming sunlight. Thus, it shows a maximum in June (Bay, 1984; Pirc, 1986; Frankignoulle & Bouquegneau, 1987). Moreover, the water column will not be homogeneous with respect to inorganic carbon caused by *Posidonia*

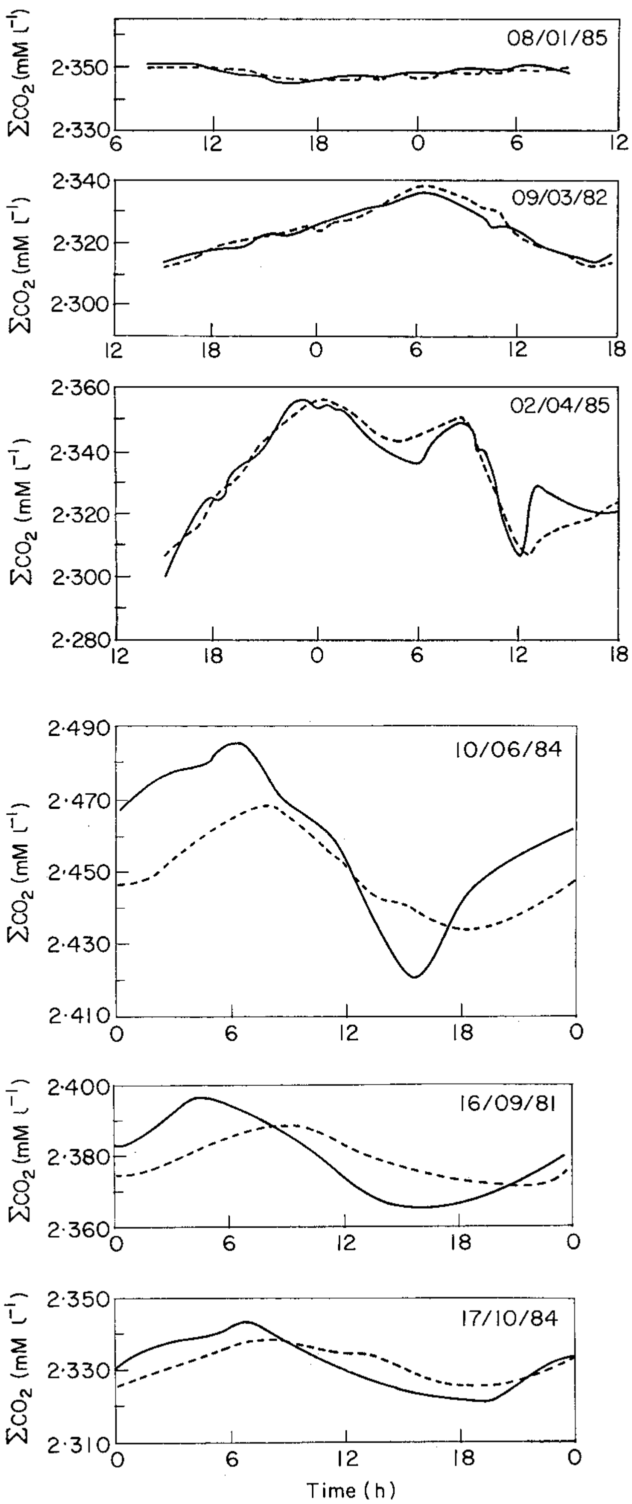

Figure 2. Daily inorganic carbon variations observed above the seagrass bed for 6 periods of the year. Bottom data are given by full lines and surface ones by dotted lines. Results of June 1984 are from Frankignoulle and Bouquegneau (1990).

activity since surface variations will depend of the transmission of the bottom variation to the surface. In fact, such differences between surface and bottom data have been exploited by Frankignoulle and Distèche (1987) to develop a simple method for the estimation of the vertical turbulence coefficient in the water column.

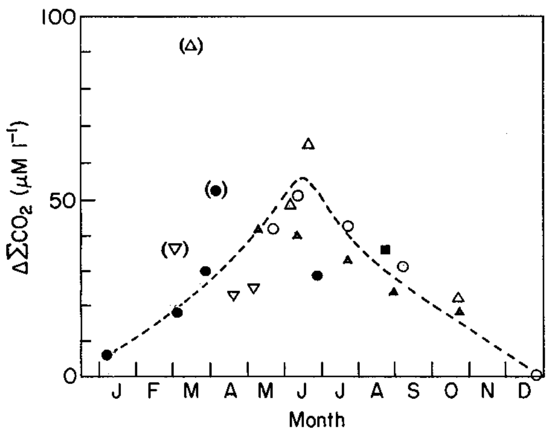

Figure 3. Seasonal course of the mean magnitude of the daily ΣCO_2 changes ($\Delta\Sigma\ CO_2$) observed above the seagrass bed in the Bay of Calvi (▲, 1980; ○, 1981; ∇, 1982; ■, 1983; △, 1984; ●, 1985).

The phytoplankton activity and the *Posidonia* seagrass bed activity should, thus, have clearly different effects on the observed inorganic carbon variations, as judged by both the homogeneity of the water column and on seasonal trend of the intensity of the variation.

Figure 2 gives some examples of surface and bottom total inorganic carbon variations recorded above the seagrass bed and for six different periods of the year covering the four seasons. The shape of the variations suggests some comments:

(i) ΣCO_2 always shows a maximum at the end of the night and a minimum at the end of the day, as would be expected if it were to be controlled by photosynthesis and respiration processes.

(ii) In January, the intensity of the variation is very low in sympathy with the reduced winter biological activity.

(iii) Both in March 1982 and in April 1985, the surface and the bottom variations are nearly the same and could thus correspond to a relatively important primary production in the water column itself.

(iv) In June, September and October, the magnitude of surface variations are lower and maxima and minima appear later than on the bottom. The implication is that the *Posidonia* seagrass bed is then the principal source of the observed CO_2 changes.

As discussed in the previous paragraph, the seasonal trend of the magnitude of the ΣCO_2 daily variations ($\Delta\Sigma CO_2$) should also allow the different phases of the biological activity to be distinguished. Figure 3 shows how $\Delta\Sigma CO_2$ changes throughout the year on the basis of measurements made during 24 campaigns in the Bay. If one omits the three data given in brackets, the values correspond to those expected for the seagrass alone, according to the results of Bay (1984) and Frankignoulle and Bouquegneau (1987): the activity of the seagrass peaks in June (maximum solar irradiance giving a high photosynthetic yield), decreases from July onwards because of the plant decay, and is relatively low in winter and in early Spring. In contrast, the phytoplankton bloom is very brief and only the campaign of March 1984 clearly coincide with a highly phytoplanktonic activity. On the basis of the observed ΣCO_2 daily variations (Figure 2), it seems that campaigns of March 1982 and April 1985 correspond to the beginning or to the end of the phenomena.

Thus, the *Posidonia* seagrass bed and phytoplankton induce regular daily total inorganic carbon variations in the water column of the Bay of Calvi the effects of which differ

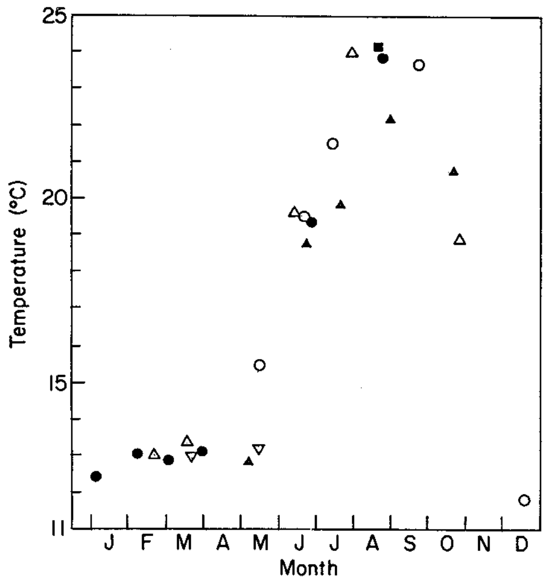

Figure 4. Seasonal course of the mean temperature observed above the seagrass bed in the Bay of the Calvi (▲, 1980; ○, 1981; ▽, 1982; ■, 1983; △, 1984; ●, 1985).

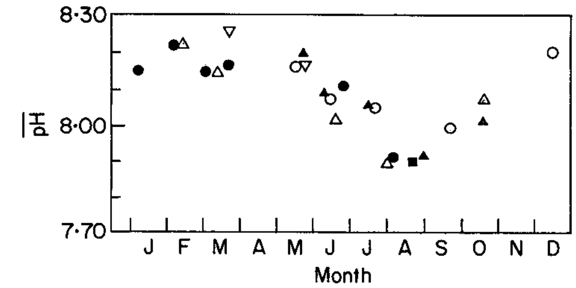

Figure 5. Seasonal course of the mean pH observed above the seagrass bed of the Bay of Calvi (▲, 1980; ○, 1981; ▽, 1982; ■, 1983; △, 1984; ●, 1985).

sufficiently, either in spatial and time distribution, to allow identification of the main primary producer.

Yearly variations

Data collected during the 24 campaigns permit testing of their seasonal reproducibility from year to year between 1980 and 1985. The seawater temperature, salinity and total alkalinity are subject to seasonal changes, but show little or no daily change.

Salinity slowly varies from 37·50‰ in winter to 38·10‰ in summer, due to evaporation and to coastal upwellings of more haline intermediate Mediterranean water.

Table 1 gives CO_2 system parameters calculated from pH and total alkalinity measurements for the 24 campaigns.

Temperature, given in Figure 4, is about 13 °C from December to the end of April, rapidly increases in May and reaches a maximum of 24 to 25 °C in September. The slope of the spring increase is +0·12 °C per day and the one of the automnal decrease is −0·10 °C per day.

The yearly variation of pH is given in Figure 5. The very good seasonal reproducibility of this parameter which shows a maximum at the end of the winter (pH = 8·25) and

TABLE 1. The CO_2 system parameters for the 24 campaigns in the Bay of Calvi, calculated from pH and TA measurements meaned on 24 hours and 8 m

	pH	TA	Σ	b	c	s	B^-	CA	*P*	S_C	S_A
May 80	8·20	2670	2391	2178	197	16	98	2571	392	407	264
Jun 80	8·09	2670	2410	2202	190	19	89	2581	549	397	258
Jul 80	8·06	2670	2422	2219	183	20	85	2585	605	383	250
Aug 80	7·92	2610	2427	2256	143	27	67	2543	885	300	197
Oct 80	8·02	2600	2371	2180	170	21	80	2519	658	356	233
May 81	8·16	2650	2374	2161	196	16	96	2554	440	410	264
Jun 81	8·08	2650	2395	2190	186	19	87	2562	571	389	253
Jul 81	8·05	2670	2417	2210	187	20	85	2584	632	392	256
Sep 81	7·98	2600	2378	2188	167	23	77	2523	761	350	230
Dec 81	8·20	2610	2341	2137	188	16	97	2513	377	393	252
Mar 82	8·26	2640	2325	2093	219	13	110	2530	329	458	294
May 82	8·17	2580	2315	2113	186	16	95	2485	413	380	240
Aug 83	7·90	2595	2412	2240	144	28	66	2528	944	302	199
Feb 84	8·23	2590	2293	2075	205	14	105	2484	345	429	275
Mar 84	8·15	2610	2356	2159	179	17	91	2518	435	374	240
Jun 84	8·02	2565	2347	2165	161	21	78	2486	648	337	219
Aug 84	7·90	2627	2445	2272	144	28	65	2561	964	302	199
Oct 84	8·08	2615	2332	2135	178	19	86	2491	552	372	242
Jan 85	8·15	2590	2348	2160	171	18	89	2501	436	357	229
Feb 85	8.22	2640	2318	2101	203	14	103	2506	357	424	272
Mar 85	8·15	2610	2359	2164	178	17	91	2519	431	372	239
Mar 85	8·18	2610	2345	2143	186	16	95	2515	408	389	249
Jun 85	7.95	2547	2365	2200	139	26	68	2478	768	291	189
Aug 85	7.91	2547	2363	2193	143	27	67	2479	898	304	201

Where: TA and CA, total alkalinity and carbonated alkalinity in $\mu eq\ l^{-1}$;
Σ, b, c, s, B^-, respectively total inorganic carbon, bicarbonate, carbonate, dissolved CO_2 and borates concentrations expressed in $\mu moles\ l^{-1}$;
P, partial CO_2 pressure in seawater expressed in 10^{-6} atm;
S_C and S_A, supersaturation with respect to calcite and aragonite in %.

minimum in August (pH = 7·90) should be noted. Frankignoulle and Distèche (1984) calculated, in a previous work and on the basis of the eight first measurements (also given in Figure 5), that about half of the yearly pH variation is due to a temperature effect (temperature dependence, $dpH\ dt^{-1}$, $-0{\cdot}012$ pH unit per degree). The seasonal reproducibility of temperature thus explain half of the pH range. However, the pH also depends on the carbonate to bicarbonate ratio (see Table 1), so each chemical, biological and physical processes that interacts with the CO_2 system modifies the pH and cyclic phenomena, e.g. the activity of the seagrass bed or the wintery mixing of water masses, are then liable with the yearly pH reproducibility.

Figure 6 shows the total alkalinity data collected during the study period and shows considerable scatter. However, accepting the 1985 data, it seems that alkalinity is higher in summer. Figure 6 also shows that the highest observed variations are about 50 $\mu eq\ l^{-1}\ month^{-1}$ (between e.g. July and August 1980) and then less then 2 $\mu eq\ l^{-1}\ d^{-1}$, which is consistent with the fact we did not observe a daily alkalinity change. Processes potentially capable of modifying alkalinity are numerous in a coastal ecosystem such as this: carbonate shell construction, dissolution of magnesian calcite (frequent in coastal water), chemical precipitation of calcite or aragonite, organic matter oxidation, coastal upwellings and currents, etc. Each of these processes is difficult to quantify but one can

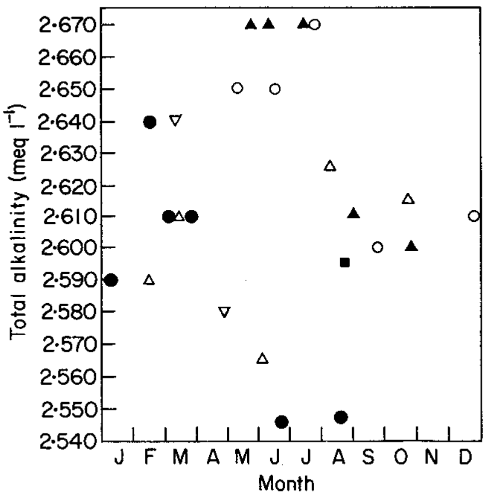

Figure 6. Seasonal course of the total alkalinity observed above the seagrass bed of the Bay of Calvi (▲, 1980; ○, 1981; ▽, 1982; ■, 1983; △, 1984; ●, 1985).

nevertheless attempt some order of magnitude calculations in order to compare the expected scatter with that shown in Figure 6:

(i) Frankignoulle and Distèche (1984) discussed the summer sudden fall in alkalinity, observed in 1980 and 1981, in terms of the sudden increase of activity of Melobesiae epiphytes. Bay (1978) estimated that such a bloom induces an increase in weight of *Posidonia* leaves of about 15% of dry weight. Assuming that the necessary carbonate is supplied by a ten meters water column, the bloom would induce a decrease of 100 ± 50 μeq l^{-1}, i.e. the order of magnitude of observed changes. One can however notice this summer decrease is not observed in 1984.

(ii) On the basis of pH, salinity and temperature measurements, one can calculate that water of the Bay is always supersaturated with respect to calcite and aragonite, respectively to about 450 to 300% in winter and 300 to 200% in summer (see Table 1, solubility coefficients given by Morse *et al.*, 1980). Chemical precipitation of 1 g of calcite per square meter and per day would induce a monthly variation of 60 μeq l^{-1} in a 10 m water column. On the other hand, during the most acidic summer conditions, the system is in equilibrium with magnesian calcite which contain 10% of magnesium (Koch, 1986). Thus, there is the possibility of an alkalinity increase arising from the dissolution of magnesium rich calcite.

(iii) The increase of salinity from winter to summer (37·5 to 38·1‰), corresponds to an alkalinity increase of about 40 μeq l^{-1}.

(iv) The Bay of Calvi is the site of complex hydrological processes which depend on local and somewhat unpredictable meteorological conditions. Thus, the decrease of alkalinity in April 1982 coincides with a cyclonic genesis period which had associated 15 to 20 m s^{-1} winds (Djenidi, 1985). More recently, Brohée *et al.* (1990) have shown that spring coastal upwellings of more haline and more alkaline water are induced in the Bay of Calvi by North-East wind of a 2–3 days duration. During their daily continuous study, they observed an increase of alkalinity of about 40 μeq l^{-1} over half a month. On the basis on the sedimentary facies, Burhenne (1981) has also suggested upwelling from the canyon situated at the entry of the Bay. Additionally, one should also note the proximity of the Liguro-Provencal thermohalin front where a cyclonic circulation induces convergence of lighter surface water, originating from the Atlantic, and divergences of deep Mediterranean water (see Hecq *et al.*, 1986).

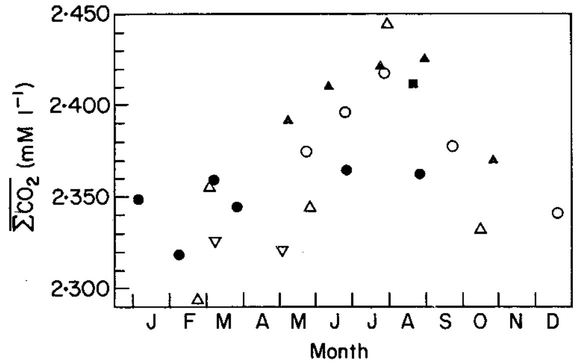

Figure 7. Seasonal course of the mean ΣCO_2 observed above the seagrass bed in the Bay of Calvi (▲, 1980; ○, 1981; ▽, 1982; ■, 1983; △, 1984; ●, 1985).

Figure 7 attempts to show the changes of total inorganic carbon throughout the year calculated on the basis of the experimental parameters described above. The ΣCO_2 concentration evolves from a mean value of 2·325 mmol l^{-1} in winter to a mean summer value of 2·425 mmole l^{-1}, with a seasonal reproducibility of 50 to 100 µmole l^{-1}. The shape of Figure 7 is difficult to interpret because CO_2 changes are induced not only by alkalinity change (with its summer maximum) but obviously also by processes using dissolved CO_2 (such as photosynthesis and respiration or air-sea CO_2 exchanges):

(i) Frankignoulle and Bouquegneau (1987) have recently shown that the *Posidonia* seagrass bed ecosystem is a sink for inorganic carbon (and a source of oxygen) from November to June and then, due to plant senescence and the increasingly important respiration, it behaves as a source of carbon (sink of oxygen) until November. These authors estimate, by integration over the year, that the seagrass ecosystem is a global annual sink of 600 tons of inorganic carbon. This value, relied to the 8×10^{11} l of water in the Bay, corresponds to a ΣCO_2 change of about 60 µmole l^{-1}.

(ii) Air-sea CO_2 exchanges have been measured in the Bay of Calvi by Frankignoulle (1988). These show that that Bay is a source of carbon for the atmosphere during nearly the whole year and with a maximum in June (about 2×10^{-7} mole of CO_2 m^{-2} s^{-1}). The integration of results proposed by Frankignoulle allows to calculate an annual decrease of about 80 µmoles l^{-1} due to air-sea exchanges.

Although quantitatively, the processes described above have an order of magnitude comparable with that of the measured curves, it is worth noticing that both the seagrass bed and the atmosphere behave as sinks of CO_2 with regard to the water column when the ΣCO_2 contents increases. Thus, as for alkalinity, the seasonal variation of total inorganic carbon is most probably mainly due to hydrodynamical processes which affect the presently unknown residence time of water in the Bay.

Conclusions

Both the *Posidonia* seagrass bed and phytoplankton induce regular daily variations of total inorganic carbon in the water column of the Bay of Calvi. Their distriution, both in space and seasonal activity, are however sufficiently different that one can distinguish the main producer by considering not only shapes of surface and bottom observed variations but also the seasonal evolution of their magnitude: phytoplanktonic activity peaks in spring and surface and bottom variations are identical, whereas the *Posidonia* activity is maximal

June and surface variation depends on the transmission of that at the bottom. Thus, except during the short period of phytoplankton bloom, the seagrass bed is responsible of the daily changes of inorganic carbon in the water column.

The seasonal development of the observed parameters has also been considered over a six years period. The reproducibility of pH value is noteworthy and one half of such seasonal pH variation as is observed is directly attributable to the effect of temperature change on pH (i.e. $dpH\,dT^{-1}$). The total inorganic carbon shows a seasonal reproducibility of about 50 μmole l^{-1} and its concentration is higher in Summer, despite the fact that both the seagrass bed and the atmosphere serve as inorganic carbon sinks. Its yearly evolution seems in fact to be mainly due to local hydrology, as also suggest by total alkalinity changes.

These investigations show that the Bay of Calvi is a site of special interest with regard to CO_2 seawater chemistry in two respects:

(i) On both daily and yearly time scales, ΣCO_2 variations are smooth and free from random or drastic changes; this is often not the case for open ocean water.

(ii) The ranges of physico-chemical conditions encountered in the Bay are particularly favourable for the study of those processes which are pH or CO_2 level dependent. Thus, the large pH range results in a surface water partial CO_2 pressure ranging between 300 ppm in winter to 1000 ppm in summer and has exploited by Frankignoulle (1988) to correlate this parameter to the air-sea CO_2 fluxes. Other topics related to the carbon cycle, for example the *in situ* chemical dissolution and precipitation of aragonite, calcite or magnesian calcite could be studied in this site, as well as diagenesis of skeletal remains in marine sediments (Poulicek *et al.*, 1990).

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