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## Field measurements of air–sea CO<sub>2</sub> exchange<sup>1</sup>

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### Abstract

The direction and magnitude of air–sea exchanges depend on the difference of gas partial pressure ( $\Delta P$ ) between phases and on a gas exchange coefficient ( $K$ ). In this work, field air–sea CO<sub>2</sub> exchange and  $\Delta P_{CO_2}$  have been measured simultaneously to study the in situ relations between parameters. Experiments have been carried out at three sites: the Bay of Calvi (Corsica), the Ligurian Sea, and the North Sea. Flux measurements were made with a direct chamber method to detect invasion or evasion of gas.

Due to its bed of seagrass (*Posidonia*), the Bay of Calvi is the site of regular, daily, and yearly variations of surface CO<sub>2</sub> content. Daily variations are often too small to overcome the variation of  $K$  and to find a correlation between hourly measured fluxes and daily changes of  $\Delta P$ . The yearly variation of  $P_{CO_2}$  in surface water (from 300 ppm in winter to 900 ppm in summer) has however permitted derivation of a linear relationship between mean fluxes and  $\Delta P$  that fits well with fluxes measured at the two other sites under similar meteorological conditions and thus with nearly the same  $K$ . Calculated coefficients range between  $10^{-5}$  and  $4 \times 10^{-5} \text{ m s}^{-1}$  and so agree well with those determined with radiotracers or in wind tunnels.

Measurements in the North Sea under different meteorological conditions show the influence of wind speed and sea state on exchanges measured by the in situ methodology used and allow the results to be compared with those obtained by others in wind tunnels.

Understanding air–sea CO<sub>2</sub> exchange is of prime importance in predicting the fate of anthropogenic CO<sub>2</sub>. The direction and magnitude of CO<sub>2</sub> flux between the aqueous and gaseous phase is described by the well-known relationship:

$$F = K\alpha\Delta P \quad (1)$$

where  $F$  is the flux ( $\text{mol m}^{-2} \text{ s}^{-1}$ ),  $\alpha$  is the

CO<sub>2</sub> solubility coefficient ( $\text{mol m}^{-3} \text{ atm}^{-1}$ ),  $\Delta P$  is the difference of CO<sub>2</sub> partial pressure between water and air (atm), and  $K$  is the gas exchange coefficient or “piston velocity” ( $\text{m s}^{-1}$ ).

Air–sea exchanges in the field are difficult to measure, and the commonly used methods, such as the ocean–atmosphere partition of tracers or the eddy correlation technique, lead to different results (e.g. Broecker et al. 1986; Smith and Jones 1986; Wesely 1986). Field measurements are also very difficult to interpret because  $K$  depends on many environmental factors such as wind speed, air and sea turbulence, presence of organic matter or hydrocarbons at the air–sea interface, formation of bubbles, etc. (e.g. Liss 1983). The  $\Delta P$  term in Eq. 1 is influenced

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by variations in  $P_{CO_2}$  in seawater or in air caused by, for example, biological activity, chemical reactions, and atmospheric and oceanic circulation.

The results of experiments carried out in the laboratory under controlled conditions are much easier to interpret. Wind tunnels have often been used to study the effect of wind speed on air-sea exchange (Kanwisher 1963; Broecker et al. 1978; Liss 1983). But extrapolation of laboratory results to the open ocean remains difficult. There is certainly a need for additional in situ and elaborate laboratory measurements in order to correlate physical and chemical events with the observed exchanges and to better understand the mechanisms of air-sea gas exchange.

The aim of my work is to study the in situ relation between air-sea  $CO_2$  exchange and  $\Delta P_{CO_2}$ . It should be linear according to Eq. 1, assuming that  $K$  is nearly constant.  $CO_2$  in surface seawater is calculated from pH and total alkalinity measurements, and the fluxes across the air-sea interface are measured by a direct method with a floating plastic bell (Sugiura et al. 1963; Frankignoulle and Distèche 1984). This method suppresses the direct wind effect (such as surface turbulence) on air-sea exchange during brief time intervals, but takes into account sea turbulence due to the sea state and exchange due to bubbling. Measurements were carried out at three sites: the oceanographic research center STARESO in the Bay of Calvi (Corsica), in the Ligurian Sea during a cruise of the RV *Recteur Dubuisson*, and in the North Sea on board the RV *Belgica*.

### Materials and methods

*Air-sea  $CO_2$  exchange and atmospheric  $CO_2$* —Air-sea  $CO_2$  exchange is determined by the direct method which consists of measuring the variation of the atmospheric  $CO_2$  level in an airtight chamber on the sea. Partial  $CO_2$  pressure contained in the air is measured with an infrared gas analyzer connected to the floating plastic bell by an air pump (Frankignoulle and Distèche 1984).

The infrared gas analyzer is the MIRAN 1-F (Foxboro Instr.), equipped with a spe-

cific filter at  $4.25 \mu m$ . The instrument is calibrated with three commercially available standard nitrogen- $CO_2$  mixtures with  $CO_2$  contents equal to 300, 350, and 400 ppm (accurate within 3%). The floating bell has a volume of  $0.4 m^3$  and a water surface of  $0.55 m^2$ .

Figure 1 gives four examples of flux measurements obtained in the Bay of Calvi in October 1984. The experiment can be divided into two main steps: before the flux measurement, the bell is kept a few minutes (until the reading from the gas analyzer is stable) above the sea surface to clean the whole system with fresh surface air and to determine its  $P_{CO_2}$  (step 1 in Fig. 1); the bell is then laid on the sea surface and the initial linear increase or decrease (step 2) of atmospheric  $CO_2$  concentration in the bell gives both the direction and magnitude of the flux. The experiment is stopped when the change becomes nonlinear (step 3). One flux measurement requires about 15 min, depending on the flux parameters.

The flux of  $CO_2$  across the sea surface is calculated according to

$$F = (\delta P_{CO_2} / \delta t)(V/RTS) \quad (2)$$

where  $F$  is the flux ( $mol CO_2 m^{-2} s^{-1}$ ),  $\delta P_{CO_2} / \delta t$  the slope ( $ppm s^{-1}$ ) of the initial variation of  $P_{CO_2}$  in the bell (step 2 in Fig. 1) calculated according to the IR gas analyzer calibration,  $V$  the volume ( $m^3$ ) of the experimental system (bell, tubes, and analyzer cell),  $R$  the gas constant ( $atm m^{-3} mol^{-1} K^{-1}$ ),  $T$  the air temperature (K), and  $S$  the water surface area in the bell ( $m^2$ ). The stability of the IR analyzer has been verified in the absence of any flux, and the limit of flux detection is  $< 10^{-8} mol CO_2 m^{-2} s^{-1}$ .

The error in the measurement is difficult to establish since it depends on many factors that are not easy to quantify. The calculation of the flux is, for example, a function of the volume of the bell, which varies during the experiment due to waves. This variation of volume will influence  $P_{CO_2}$  in the bell. However, waves have a short characteristic period relative to that required for the experiment, and their influence is most probably negligible on the global flux measurement, especially since waves act in an

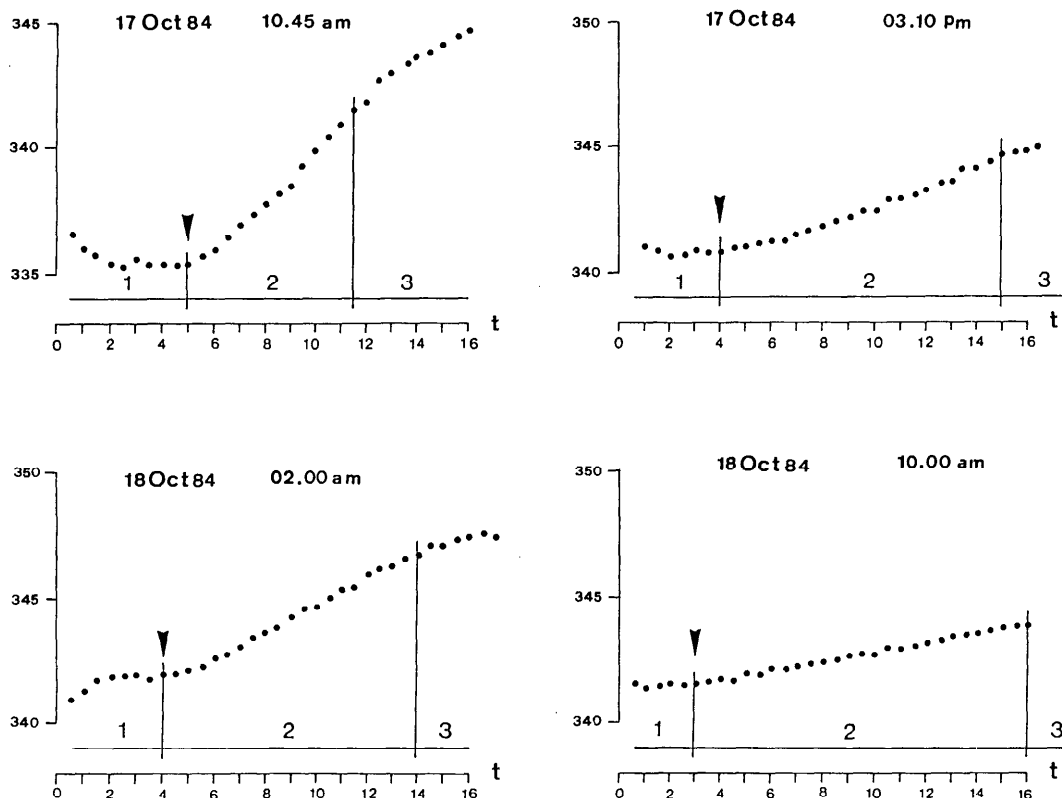


Fig. 1. Some examples of the direct measurements of air-sea  $\text{CO}_2$  exchange obtained in the Bay of Calvi. Abscissa—time in minutes; ordinate— $P_{\text{CO}_2}$  in the bell, expressed in ppm. Experiments are divided in three steps, as discussed in text. Arrowheads—time at which the bell is laid down on the sea surface.

oscillating manner on the volume. In any case, I estimate that the relative error does not exceed 25%.

**Seawater  $\text{CO}_2$  chemistry**—The  $P_{\text{CO}_2}$  and the  $\text{CO}_2$  speciation in the surface water are calculated from pH and total alkalinity measurements (Frankignoulle and Distèche 1984). Direct total inorganic carbon controls have been made under laboratory conditions in order to test the coherence between the calibration techniques and equilibrium constants chosen for carbonic and boric acids.

I use the sea-going electrode (Distèche 1959, 1962, 1964), which is pressure compensated and built to minimize the junction potential. The inner glass electrode solution is 0.01 N HCl with NaCl added to increase the ionic strength to 0.650. Distèche and

Distèche (1967) have shown that such a solution has a  $\text{pH} = 2 \pm 0.01$ . The Nernst slope of the electrode is determined by titrating a solution of 0.01 N  $\text{Na}_3\text{PO}_4 + \text{NaCl}$  (ionic strength adjusted to 0.650 with NaCl). The absolute pH value is measured with a precision of 0.01 pH unit, and the stability of the electrochemical cell allows detection of variations as small as 0.001 pH unit.

Total alkalinity (TA) is determined with the titration method proposed by Gran (1952). After degassing the sample, pH is measured for seven HCl additions spanning the equivalence point. The extrapolation of the Gran function (corrected for fluorides and sulfates: Hansson and Jagner 1973) to zero gives the equivalence point. The precision of the method, established with standard  $\text{Na}_2\text{CO}_3$  solutions, is 0.2%.

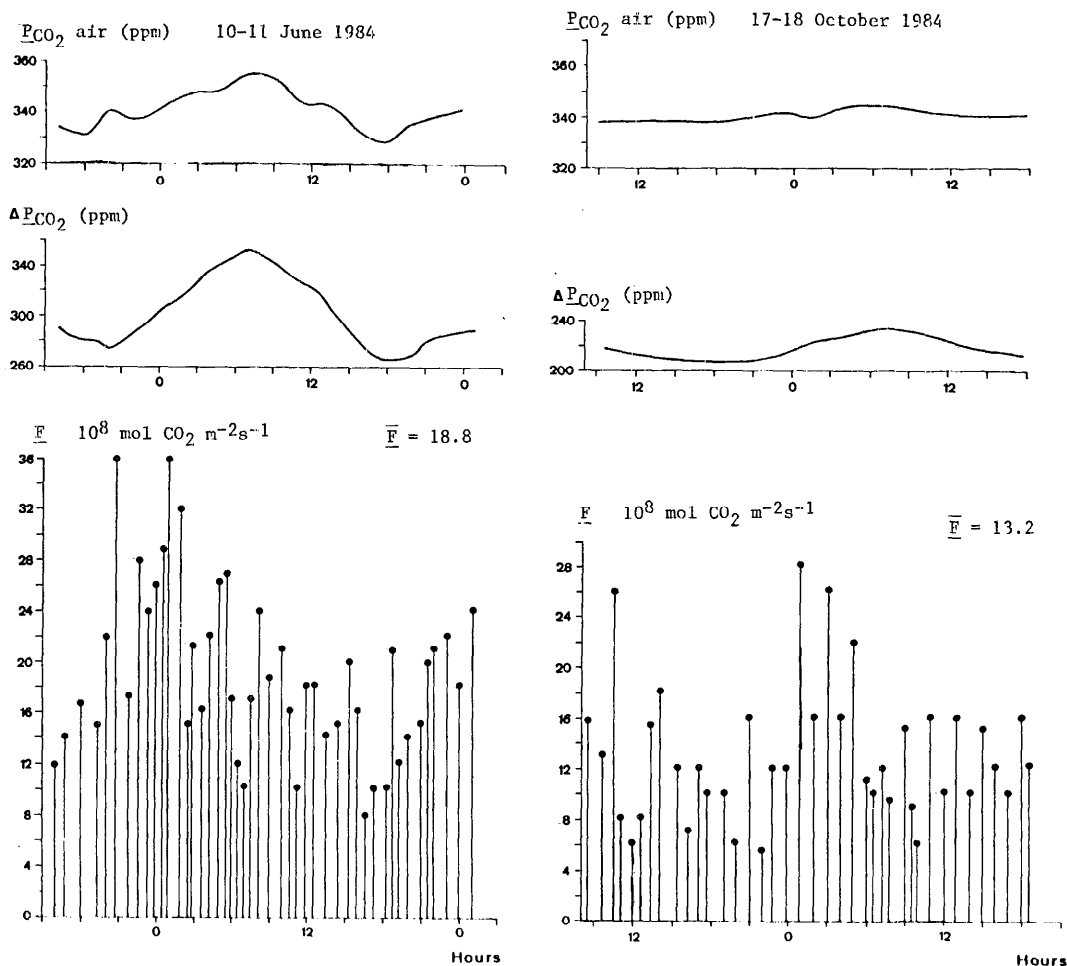


Fig. 2. Daily variations of measured atmospheric  $P_{CO_2}$ ,  $\Delta P_{CO_2}$  between sea and air, and air-sea  $CO_2$  exchange ( $F < 0$  for air-sea flux) in the Bay of Calvi.

The  $CO_2$  speciation is calculated with the dissociation constants of Mehrbach et al. (1973) for carbonic acid and of Lyman (1957) for boric acid. The  $CO_2$  solubility coefficient of Weiss (1974) is used to calculate the seawater partial pressure. These constants are corrected for salinity and temperature. Borate concentration is calculated from the borate:salinity ratio of Culkin (1965).

The precision obtained for the calculated  $P_{CO_2}$  in seawater with pH and TA measurements is within 3%, using laboratory determinations of total inorganic carbon. This order of magnitude is comparable to

the inaccuracy of the gas standard mixtures used to calibrate the IR analyzer for  $P_{CO_2}$  in air. One can also calculate that the stability of the pH cell allows detection of variations  $< 3$  ppm in  $P_{CO_2}$ .

#### Results and discussion

The Bay of Calvi is a particularly interesting site to study air-sea  $CO_2$  exchange as a function of seawater  $CO_2$  chemistry since the *Posidonia* seagrass bed induces very regular, sometimes nearly sinusoidal, daily variations of total inorganic carbon and  $P_{CO_2}$  in surface seawater. The range of variation of this daily signal is a function of the sea-

Table 1. Nighttime and daytime averages of measured CO<sub>2</sub> fluxes ( $\pm$ SD) in the Bay of Calvi and differences between night maxima ( $\Delta P_M$ ) and day minima ( $\Delta P_m$ ) of  $\Delta P_{CO_2}$ .

	Flux* averages		$(\Delta P_M - \Delta P_m)^\dagger$
	Night	Day	
9 Jan 85	12.1 $\pm$ 3.3	11.9 $\pm$ 3.5	9
4 Feb 84	-8.8 $\pm$ 4.0	-7.3 $\pm$ 3.5	16
28 Feb 84	15.6 $\pm$ 3.8	5.7 $\pm$ 2.7	158
3 May 82	6.0 $\pm$ 4.3	6.0 $\pm$ 4.5	40
11 Jun 84	20.4 $\pm$ 4.3	17.0 $\pm$ 4.7	77
22 Aug 83	6.5 $\pm$ 3.2	7.2 $\pm$ 3.2	65
18 Oct 84	14.0 $\pm$ 4.6	12.5 $\pm$ 4.4	27

\* Expressed in  $10^{-8}$  mol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>.

† In ppm ( $10^{-6}$  atm).

sonal activity of the seagrass bed: it is near zero in winter and reaches about 100 ppm in June. Preliminary work (Frankignoulle and Distèche 1984) indicates that hourly CO<sub>2</sub> flux measurements show scatter that does not permit correlation of the flux magnitudes with daily variation of the  $P_{CO_2}$  of the seawater. This scatter was attributed to variation in the forcing function influencing  $K$  due, for example, to waves, turbulence, bubbling of oxygen, and surface films. Sudden wind variations cannot explain this scatter, since the wind was steady most of the time and its speed was always  $<3$  m s<sup>-1</sup> (i.e. the range of wind speed over which  $K$  varies gradually: Liss 1983). Daily variations of  $\Delta P$  are thus too small, relative to those of  $K$ , to find a relation between measured fluxes and  $\Delta P$ .

Figure 2 shows an example of hourly measured fluxes, the atmospheric CO<sub>2</sub> level, and the  $\Delta P_{CO_2}$  between both phases in June and October 1984. It appears that scatter is large in both cases, but in June, when the activity of the *Posidonia* bed (and thus also the daily change of  $P_{CO_2}$  in seawater) is maximal, daytime fluxes are obviously lower than those at night, although maxima of fluxes and  $\Delta P$  are not well correlated. To illustrate this, Table 1 gives day and night averages of measured fluxes for several periods in the Bay of Calvi compared to the diel variation of  $\Delta P$  (i.e. the difference between the nocturnal maximum and the diurnal minimum of  $\Delta P$ ). Table 1 shows a clear difference between day and night measurements in February 1984 during a phy-

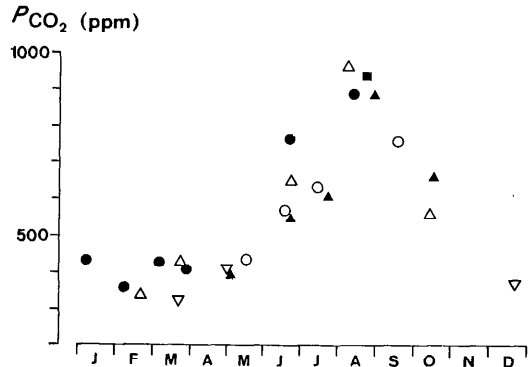


Fig. 3. Seasonal variation of  $P_{CO_2}$  in the surface seawater of the Bay of Calvi:  $\blacktriangle$ —1980;  $\circ$ —1981;  $\nabla$ —1982;  $\blacksquare$ —1983;  $\triangle$ —1984;  $\bullet$ —1985.

toplankton bloom that induced a relatively important daily CO<sub>2</sub> change in the surface water. For all the other periods measured, the range of daily chemical conditions is smaller than the variation in  $K$ , and thus the magnitude of the flux is not well correlated with  $\Delta P$ .

The annual variation of  $P_{CO_2}$  of the surface seawater of the Bay of Calvi follows a regular pattern and covers a much larger range of chemical conditions. This is well illustrated in Fig. 3, which gives  $P_{CO_2}$  in the surface water between 1980 and 1985: the  $P_{CO_2}$  of surface water regularly varied annually between about 300 and 900 ppm. The measurement series in the North Sea permitted extension of the range of observations to about 200 ppm for the  $P_{CO_2}$  of water (Table 2). The Bay of Calvi is a source of CO<sub>2</sub> to the atmosphere, except at the end of winter when  $\Delta P_{CO_2}$ , although small, remains positive. The Ligurian Sea acts as a source in June, and the North Sea is a relatively important sink in April. Table 2 further shows that the fluxes measured in August are relatively low despite the maximal  $\Delta P_{CO_2}$ .

If one omits the August results (cf. later discussion at slicks), one finds a linear relationship (Fig. 4) between the observed mean fluxes and  $\Delta P_{CO_2}$ . Vertical lines in Fig. 4 indicate the range of flux values obtained. Those lines do not correspond to the experimental error but to variation in the in situ measurement. By forcing the

Table 2. Experimental surface seawater and air-sea flux data.

	pH	TA*	$\Delta P$ †	$F$ ‡	No.§
Bay of Calvi					
9 Jan 85	8.15	2.590	96	12.0±3.4	28
4 Feb 84	8.23	2.590	5	-8.0±3.7	42
28 Feb 84	8.15	2.610	95	10.3±6.4	26
11 Mar 85	8.15	2.610	91	7.0±2.1	21
3 May 82	8.17	2.580	86	6.0±4.4	28
11 Jun 84	8.02	2.565	308	18.8±6.6	46
22 Aug 83	7.90	2.595	604	6.9±3.2	30
1 Aug 84	7.90	2.627	624	3.2±3.0	34
16 Aug 85	7.91	2.547	558	12.0±4.0	14
18 Oct 84	8.08	2.610	212	13.2±4.5	38
15 Dec 81	8.20	2.610	37	0	31
Ligurian Sea					
12 Jun 84	8.11	2.611	171	9.1±2.1	8
19 Jun 85	8.04	2.581	268	7.8±2.2	5
North Sea (Shetland Islands)					
26 Apr 85	8.36	2.350	-220	-14.9±3.1	10

\* Total alkalinity in meq liter<sup>-1</sup>.

† Difference of  $P_{CO_2}$  between sea and air in ppm ( $10^{-6}$  atm; the  $P_{CO_2}$  air was always  $340 \pm 10$  ppm).

‡ The flux from sea to air ( $\pm$ SD) in  $10^{-8}$  mol  $CO_2$   $m^{-2}$   $s^{-1}$ .

§ Number of flux measurements.

regression through zero, the relationship between the flux and  $\Delta P_{CO_2}$  can be written:

$$F = 7.0 \times 10^{-4} \Delta P_{CO_2} \quad (3)$$

(11 points,  $r = 0.87$ ;  $P < 0.01$ )

where flux is expressed in mol  $CO_2$   $m^{-2}$   $s^{-1}$  and  $\Delta P_{CO_2}$  in atm.

Note that, according to the experimental data, a value of  $\Delta P_{CO_2}$  equal to zero corresponds to a flux from air to sea, but the uncertainty is large enough that this flux is not significantly different from zero, and Eq. 3 can be written. One can, however, stress the relatively important air-sea flux measured in February 1984, where  $\Delta P_{CO_2}$  is nearly zero and should thus induce only a small flux. By taking the experimental error in  $P_{CO_2}$  into account (i.e. 3%), Eq. 3 indicates that the maximum influx in February 1984 should be  $-3 \times 10^{-8}$  mol  $m^{-2}$   $s^{-1}$ , i.e. a third of the observed value. The other negative flux, obtained in April 1985 in the North Sea, is also well off the line in Fig. 4. As discussed above, the data are insufficient to identify the mechanisms responsible for these variations.

From the measured flux and the  $\Delta P_{CO_2}$ , one can calculate the related  $K$  (piston velocity) from Eq. 2 and 3. Values, given in

Table 3, range between  $10^{-5}$  and  $4 \times 10^{-5}$   $m$   $s^{-1}$ . The February 1984 value is calculated with  $\Delta P$  and flux data of opposite signs (see Table 2). The slope of the line given in Fig. 4 allows calculation, using the average solubility coefficient  $\alpha$  (i.e. 39 mol atm<sup>-1</sup>  $m^{-3}$ ), of a mean value of  $K$  equal to  $1.8 \times 10^{-5}$   $m$   $s^{-1}$  for a wind speed of 3  $m$   $s^{-1}$ . Results presented here are thus in agreement with those obtained by other workers during laboratory experiments (wind tunnels) or using the ocean-atmosphere partition of radiocarbon or <sup>222</sup>Rn. Broecker et al. (1980) reviewed the results obtained in situ and gave values from  $0.7 \times 10^{-5}$  to  $9.6 \times 10^{-5}$   $m$   $s^{-1}$ . The results of Peng et al. (1979) for the GEOSECS program in the Atlantic and the Pacific give a mean value of  $3.1 \times 10^{-5}$   $m$   $s^{-1}$  and Johnson et al. (1979) calculated  $K$  equal to  $2.2 \times 10^{-5}$   $m$   $s^{-1}$  for Stuart Channel (British Columbia). Sugiura et al. (1963) found  $4 \times 10^{-5}$   $m$   $s^{-1}$  in the Gulf of Mexico, using the same direct method as mine. Liss (1983) compared all the available results and proposed a global value of  $5.6 \times 10^{-5}$   $m$   $s^{-1}$ , corresponding to a mean wind speed of 6  $m$   $s^{-1}$  according to the results from wind tunnels.

The data presented thus disagree with those obtained with the eddy correlation

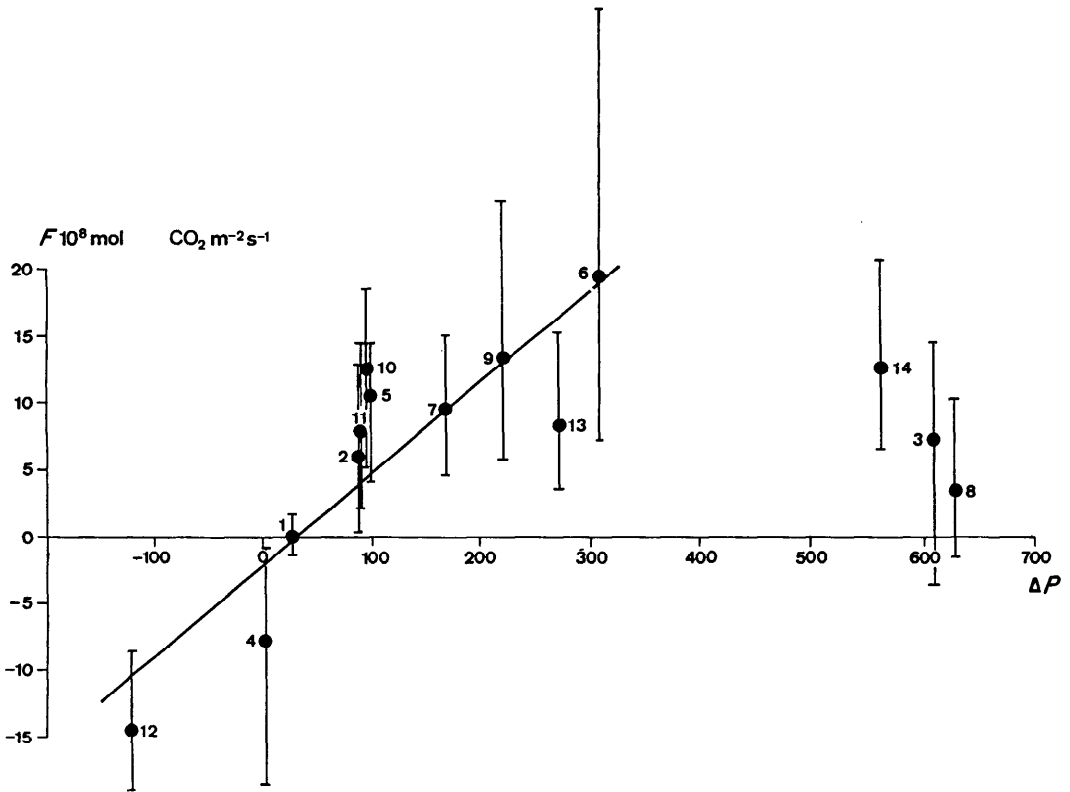


Fig. 4. Measured mean air-sea CO<sub>2</sub> fluxes as a function of  $\Delta P_{CO_2}$  between sea and air. The line does not take into account points 3, 8, and 14. Data from Table 2. 1—December 1981; 2—May 1982; 3—August 1983; 4—February 1984; 5—March 1985; 6—June 1984; 7—June 1984, Ligurian Sea; 8—August 1984; 9—October 1984; 10—January 1985; 11—March 1985; 12—April 1985, North Sea; 13—June 1985, Ligurian Sea; 14—August 1985.

technique—the other direct in situ methodology, first applied to CO<sub>2</sub> by Jones and Smith (1977)—which gives  $K$  values about one order of magnitude greater than those discussed above. This conflict is of prime importance (Broecker et al. 1986; Smith and Jones 1986; Wesely 1986). Although horizontal atmospheric advection is probably the most important error source in eddy correlation, the defenders of this technique argue that short-term and local phenomena (such as bubbles, spray, and waves; Smith and Jones 1985) would have a strong influence on air-sea exchange which is not detected by long-term partition studies. It is worth noting that my methodology gives results in better agreement with ocean tracers, takes account of most of the short-term and local events in the water col-

umn, and, due to the bell, is unaffected by atmospheric advection.

Table 3 also gives the calculated thicknesses of the boundary layer through which the transfer of CO<sub>2</sub> is assumed to be made by molecular diffusion (stagnant film model; Whitman 1923). The values obtained, calculated with the molecular diffusivity coefficient given by Broecker and Peng (1982) ( $10^{-9}$  m<sup>2</sup> s<sup>-1</sup> at 0°C and  $1.9 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup> at 24°C), are in good agreement with those in the literature (Skirrow 1975: 50–300  $\mu$ m; Broecker and Peng 1982: mean value of 40  $\mu$ m from the ocean-atmosphere distribution of <sup>14</sup>C and <sup>222</sup>Rn).

During the experiments presented in Table 2 and Fig. 4, the sea state was always calm (waves <0.3 m) and the wind speed was always <5 m s<sup>-1</sup> and more often <3

Table 3. Calculated values ( $\pm$ SD) of gas exchange coefficient ( $K$ ) and thicknesses of the surface microlayer ( $Z$ ).

	$K$ ( $10^{-5} \text{ m s}^{-1}$ )	$Z$ ( $\mu\text{m}$ )
Bay of Calvi		
9 Jan 85	$3.6 \pm 1.0$	$48 \pm 12$
4 Feb 84	$3.8 \pm 1.6$	$55 \pm 20$
28 Feb 84	$3.3 \pm 2.0$	$56 \pm 30$
11 Mar 85	$2.5 \pm 0.8$	$79 \pm 30$
3 May 82	$2.4 \pm 1.5$	$84 \pm 50$
11 Jun 84	$2.1 \pm 0.7$	$94 \pm 30$
16 Oct 84	$2.2 \pm 0.7$	$92 \pm 30$
Ligurian Sea		
12 Jun 84	$2.0 \pm 0.5$	$93 \pm 25$
19 Jun 85	$1.1 \pm 0.3$	$200 \pm 50$
North Sea		
26 Apr 85	$2.1 \pm 0.4$	$51 \pm 10$

$\text{m s}^{-1}$  in both the Mediterranean Sea and in the North Sea. Results obtained in wind tunnels by some workers and cited by Liss (1983) show that  $K$  is in fact nearly constant in this range of low wind speed. The direct method takes into account the effect of water-column turbulence on air-sea exchange. Frankignoulle and Distèche (1987) have recently shown that the transmission of the daily inorganic carbon variation from the bottom to the surface, induced by the *Posidonia* bed of the Bay of Calvi, permits calculation of the vertical turbulent diffusion coefficient in the water column. During three measurement series, this diffusion coefficient and the gas exchange coefficient were determined simultaneously. Although differences are not statistically significant, the most turbulent case (May 1982) corresponds with the highest value of  $K$  (Table 4). Further experiments should be carried out to correlate both coefficients.

Some results obtained in the North Sea are especially interesting to study the response of my methodology to effects of wind and sea state. During the RV *Belgica* cruise in April 1985, I made flux measurements under five different meteorological conditions. Table 5 gives gas exchange coefficients obtained in situ by the direct method and by values calculated on the basis of the wind tunnel results of Broecker et al. (1978). In case 1, the results are similar due to the

Table 4. Gas exchange ( $K$ ) and turbulence coefficients in the Bay of Calvi.

	$K$ ( $10^{-5} \text{ m s}^{-1}$ )	Turbulence coefficient ( $10^{-3} \text{ m}^2 \text{ s}^{-1}$ )
May 82	2.4	16
Jun 84	2.1	8
Oct 84	2.1	7

low wind speed and calm sea state. This case is the one I have chosen to compare to the results obtained in the Mediterranean Sea (Table 2) because of the similarity of meteorological conditions and the consequent similarity of gas exchange coefficients. In case 2, a sudden high wind burst occurred that did not induce a rough sea at first (wind coming from the land) but generated strong wind drifts. One can see that the direct method clearly indicates a strong increase of the flux, but it is lower than the one obtained in the wind tunnel. It is obvious that such a wind speed induces a high level of turbulence in the surface seawater, the effect of which is detected by my method. Effects of turbulence in the air and at the interface (such as capillary waves) are, however, suppressed by the bell and one finds a lower value. Case 3 is particularly interesting in terms of wind speed and associated sea state. In spite of a low wind, the sea is rough and the coefficient obtained in situ is 2–3 times higher than the one obtained in a wind tunnel, because the methodology takes into account the turbulence related to sea state. This observation clearly illustrates the difficulty of applying laboratory results to the field: the effects of fetch and wind duration on sea state are not easily simulated. Cases 4 and 5 illustrate once again the previous observations: a high wind corresponds to a lower in situ value (4) but, if it persists, induces a modification of sea state which is detected by the direct method (5). The results in the North Sea thus clearly show the advantages and disadvantages of both in situ and laboratory methodologies in studying the influences on air-sea exchange.

The anomalies observed in August in the Bay of Calvi could correspond to a decrease of the exchange coefficient. As shown in Fig. 4, the measured fluxes in August are



Table 5. Meteorological conditions and related gas exchange coefficients (*K*) in the North Sea.

Case*	Wind speed (m s <sup>-1</sup> )	Sea state	Flux†	<i>K</i> ‡ (10 <sup>-5</sup> m s <sup>-1</sup> )	
				In situ	Wind tunnel
1	1-3	Calm	-14.9±3.1	2.1	1-2
2	14	Smooth (strong wind drift)	-79±12	13.4	19
3	3-4	Rough	-39±8	6.6	2-3
4	7-8	Rough	-46±9	7.8	8-10
5	7-8	Very rough (3-m waves)	-63±11	10.7	8-10

\* Cases 1 and 2 in the Shetland Islands (Hoswick Bay 59°59'N, 01°15'W), cases 3, 4, and 5 at 54°00'N, 02°00'E.

† In 10<sup>-9</sup> mol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> ± SD.

‡ In situ from this work, in wind tunnel from Broecker et al. 1978.

about four times less than expected from Eq. 2, and *K* corresponding to those fluxes is about 0.5 × 10<sup>-5</sup> m s<sup>-1</sup>.

In August, events were observed that are liable to decrease the value of the coefficient or to alter the flux measurement. There was a condensation on the inner face of the bell, which might trap CO<sub>2</sub> and thus mask a small part of the exchange. Second, the human population of the Bay of Calvi drastically increases in summer (3,500 inhabitants in winter and about 35,000 in summer), which should induce an important increase of hydrocarbon spills and organic matter discharge that could modify the air-sea interface and decrease the exchange coefficient. Surface slicks were sometimes observed and further experiments must be carried out to study the yearly variation of surface seawater properties. Third, in correspondence with the clearly different sea state, the turbulence of the surface water is often lower in summer, due to both wind direction (the so-called Libeccio, a southwest wind, is dominant in summer; see Loffet 1978) and nearly absent wind speed. Those observations are only qualitative, and anomalously low fluxes obtained in August in the Bay of Calvi are not well understood. A more appropriate study is necessary to quantify each factor liable to decrease *K*.

The goal of this work was not to bring a response to the serious controversy in oceanic CO<sub>2</sub> fluxes but to contribute to the need for data and methods necessary to understand this complex and important multidisciplinary problem. I am fully aware of the limits and defects of my methodology, such as the difficulty of using the bell in severe weather, but especially the loss of precision and the doubt concerning appli-

cability close to the ocean-atmosphere PCO<sub>2</sub> equilibrium condition.

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