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THE SEAWATER HOMOGENOUS BUFFER FACTOR. ITS IMPORTANCE IN THE  
PHYSICO-CHEMICAL STUDY OF AIR-SEA CO<sub>2</sub> EXCHANGES.

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ABSTRACT

The calculations of the homogenous buffer factor  $\beta_h = \left(\frac{\partial P}{\partial \Sigma}\right)_w$  (P partial pressure of CO<sub>2</sub>,  $\Sigma$  total inorganic carbon, in water w) is given for three regimes : constant carbonate concentration, constant carbonate alkalinity, constant total alkalinity.

There is experimental evidence showing that the CO<sub>2</sub> air-sea and outflux linearly depend on  $\beta_{hTA}$  in coastal mediterranean waters. Mapping  $\beta_{hTA}$  of surface waters would correspond to mapping corresponding sinks or sources of CO<sub>2</sub>.

Monitoring of pH and  $\beta_h$  is recommended to evaluate the capacity of a marine region to buffer atmospheric CO<sub>2</sub> increases.

The understanding of the air-sea CO<sub>2</sub> exchange mechanism is important in order to construct models to predict the fate of the atmospheric CO<sub>2</sub> level.

The parameters which govern these exchanges are numerous, often difficult to determine and generally with little known relative importance : turbulence in air and sea near/at the interface ; flora and fauna living near/at the interface ; CO<sub>2</sub> concentration in both phases ; carbonate dissolution or precipitation, mixing of water masses,...

The effect of many of the chemical parameters can be condensed into one factor, the homogenous buffer factor.

### THEORETICAL CONSIDERATIONS

The capacity of the ocean to buffer an increase of the atmospheric CO<sub>2</sub> level has been defined in terms of a buffer factor  $\beta$  (BROECKER *et al.*, 1971 cited by SKIRROW, 1975)

$$\beta = \left(\frac{\delta P}{P}\right)_a \left(\frac{\partial \Sigma}{\Sigma}\right)_w^{-1} \quad (1)$$

where  $\beta$  = buffer factor

P = atmospheric partial CO<sub>2</sub> pressure

$\Sigma$  = total inorganic carbon in seawater

$\beta$  relates the variation of the atmospheric partial CO<sub>2</sub> pressure ( $\delta P$ ) to a variation ( $\partial \Sigma$ ) of the inorganic carbon in seawater in a very simple way. SKIRROW (1975) and PYTKOWICZ and SMALL (1977) have discussed this relation and come to the conclusion that if the entirety of the ocean reservoir is theoretically able to buffer four-fifths of the actual CO<sub>2</sub> increase, only ten percent can be taken up by the mixed layer. The global buffer capacity of the ocean thus mainly depends on the time of mixing of the water masses.

The buffer factor as defined above can be evaluated from a knowledge of the CO<sub>2</sub> chemistry and distribution in both phases.

If one restricts oneself to the aqueous phase, it is possible to define another buffer factor, called the homogenous buffer factor ( $\beta_h$ ) as follows :

$$\beta_h = \left(\frac{\partial P}{P}\right)_w \left(\frac{\partial \Sigma}{\Sigma}\right)_w^{-1} \quad (2)$$

where P is the partial CO<sub>2</sub> pressure in seawater  
 Σ is the total inorganic carbon in seawater

If - at equilibrium between gas and liquid phases - the partial CO<sub>2</sub> pressure in seawater is equal to the partial CO<sub>2</sub> pressure in the atmosphere, β<sub>h</sub> = β.

The so defined homogenous buffer factor can be calculated by taking into account the instantaneous physico-chemical properties of a given seawater :

$$\text{since } \Sigma = s + b + c \quad (3)$$

with  $s = [\text{CO}_2^*]$  = dissolved CO<sub>2</sub> molar concentration

$b = [\text{HCO}_3^-]$  = bicarbonate molar concentration

$c = [\text{CO}_3^{=}]$  = carbonate concentration

we can write

$$\beta_h = \frac{\Sigma}{s} \cdot \frac{\partial s}{\partial \Sigma} \quad (4)$$

$$\text{and, therefore, } \beta_h = \frac{(s+b+c)}{s} \cdot \frac{\partial s / \partial H}{\frac{\partial s}{\partial H} + \frac{\partial b}{\partial H} + \frac{\partial c}{\partial H}} \quad (5)$$

where  $H = [\text{H}^+] = 10^{-\text{pH}}$

From the chemical equilibria of carbonic acid in seawater (MILLERO, 1979)

$$s = \frac{AH^2}{K_1(H+2K_2)} \quad (6)$$

$$b = \frac{AH}{H+2K_2} \quad (7)$$

$$c = \frac{AK_2}{H+2K_2} \quad (8)$$

where A = carbonate alkalinity = b + 2c

K<sub>1</sub>, K<sub>2</sub> = dissociation constants of carbonic acid in seawater  
 (MERBACH *et al.*, 1973)

$$\text{So, } \frac{\partial s}{\partial H} = \frac{AH(4K_2+H) + (2K_2+H)H^2 \frac{\partial A}{\partial H}}{K_1(2K_2+H)^2} \quad (9)$$

$$\frac{\partial b}{\partial H} = \frac{2K_2A + (2K_2+H)H \frac{\partial A}{\partial H}}{(2K_2+H)^2} \quad (10)$$

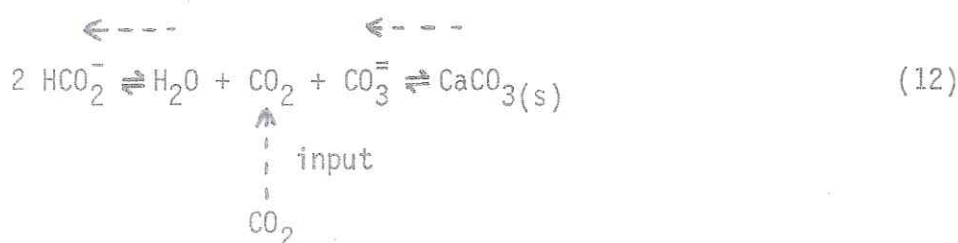
$$\frac{\partial c}{\partial H} = \frac{-K_2 A + (2K_2 + H)K_2 \frac{\partial A}{\partial H}}{(2K_2 + H)^2} \quad (11)$$

The calculation of  $\beta_h$  requires the determination of each term given in equations (6) to (11) :

- $K_1$  and  $K_2$  are calculable as functions of the temperature and salinity from data given in the literature (see MILLERO, 1979)
- H and A are experimentally accessible (see f.ex. FRANKIGNOULLE and DISTECHE, 1984)
- the speciation of the  $CO_2$  system (s, b and c) is calculable from eq. (6) to (8)
- partial H derivatives of s, b and c (eq. (9) to 11)) could thus be calculated assuming the determination of  $\frac{\partial A}{\partial H}$ , but this last term can be expressed analytically for several thermodynamical constraints as discussed by McINTYRE (1978) and SUNDQUIST *et al.* (1979) and presented here in a somewhat different way.

First constraint : the carbonate concentration is constant

If we consider the chemical equilibrium of  $CO_2$  in seawater (eq. (12)), it appears that keeping the carbonate concentration constant, during an input of dissolved  $CO_2$ , needs a quantitative dissolution of the solid carbonate phase (dotted line)



This quantitative dissolution can only occur as far as thermodynamical and kinetical conditions permit.

The thermodynamical condition implies that the ionic product ( $[Ca^{2+}] \cdot [CO_3^{2-}]$ ) must be lower than the solubility constant of  $CaCO_3$  in seawater, that is the system must be undersaturated. Now the surface seawaters, in the actual range of pH, are supersaturated with respect to calcite and aragonite. This fact excludes any dissolution. Coastal seawater can however be in equilibrium with magnesian calcites ( $Mg_x Ca_{1-x} CO_3$ , where  $x = 0.10 - 0.15$  and higher ; see KOCH,

1984)), which are more soluble than calcite and aragonite. The relative abundance of the magnesian calcites, versus calcite and aragonite is known with precision.

The kinetical condition is a very complex problem since biogenic solid carbonates are always inbedded in an organic matrix the destruction of which delays dissolution in a generally unknown way.

Authygenic carbonate particles or deposits can be abundant in lagoons where very large pH shifts are observed. The dissolution-precipitation process is however complicated by the fact that the precipitated carbonates are never homogenous. The redissolution is also kinetically controlled.

The carbonate constant constraint is equated as follows :

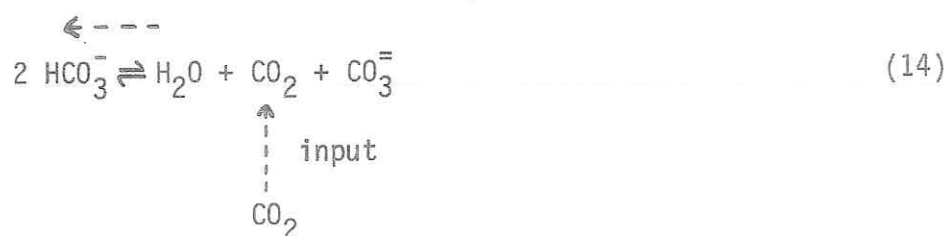
since  $A = b+2c$  and  $c = \text{constant}$

$$\text{then } \frac{\partial A}{\partial H} = \frac{\partial b}{\partial H} \quad (13)$$

Equation (13) allows to solve eq. (9) to (11) and thus to calculate the homogenous buffer factor at constant carbonate concentration  $\beta_{hc}$ .

Second constraint : the carbonate alkalinity is constant

If the carbonate alkalinity is constant, the buffering of an input of dissolved  $\text{CO}_2$  excludes any exchange with the solid phase :



Since the reaction of one  $\text{CO}_2$  with one carbonate gives two carbonates, the carbonate alkalinity (see above) keeps unchanged.

The calculation of the homogenous buffer factor at carbonate alkalinity constant  $\beta_{hA}$  is easy since  $\frac{\partial A}{\partial H} = 0$ .

Third constraint : the total alkalinity is constant

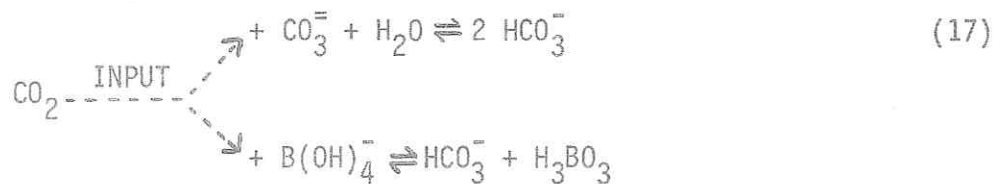
The total alkalinity (TA) is defined by

$$TA = A + B^- \quad (15)$$

where  $B^-$  is the excess of weak bases in seawater other than those of the carbonate system (included in A).  $B^-$  is essentially borate and eq. (15) becomes

$$TA = A + B(OH)_4^- \quad (16)$$

This constraint is similar to the second one but takes into account the buffering effect of borates :



A change in  $\text{CO}_2$  does not affect TA and does not imply exchange with the solid phase.

This third constraint is equated as follows :

$$\text{if } TA = A + B(OH)_4^-$$

$$\text{then } \frac{\partial A}{\partial H} = \frac{\partial B(OH)_4^-}{\partial H} = \frac{K_B + TB}{(K_B + H)^2} \quad (18)$$

where  $K_B$  = dissociation constant of boric acid (LYMAN, 1957 cited by MILLERO, 1979)

T.B. = total borate in seawater =  $1.212 \cdot 10^{-5}$  x salinity (CULKIN, 1965)

$\beta_{hTA}$  follows from equations (5)(9-11).

Fig.1 (adapted from FRANKIGNOULLE and DISTECHE, 1984) gives the dependence of the calculated buffer factor  $\beta_h$  on pH ( $S\%_o = 38$  ;  $t = 20^\circ\text{C}$  ;  $A = 2.6 \text{ meq.l}^{-1}$  at pH 8 for coastal mediterranean water). The dissolution of calcite can thermodynamically occur at pH = 7.7 and that of Mg-calcite (10-15% of Mg) at about pH = 7.9 (see EDMOND and GIESKES, 1970 ; MORSE *et al.*, 1980 ; WOLLAST *et al.*, 1980). At pH > 7.9 the system can safely be assumed to behave at constant total alkalinity. Mg-calcites of Mg content > 15% are present but

their relative abundance is low. At  $\text{pH} < 7.7$  the system is theoretically at constant carbonate regime assuming that solid carbonates readily dissolve. The range of transition between both regimes (T.A. constant and C constant) is stippled on the figure to show that the behaviour of the system depends on the availability of carbonates which depends on rate processes.

Fig.1 shows very well that the carbonate constant constraint highly increases the capacity of seawater to buffer a  $\text{CO}_2$  increase in the atmosphere (see eq. (1) and (2) ; as  $\beta$  decreases, the buffer effect increases) simply because  $\text{CO}_2$  now reacts with solid carbonates.

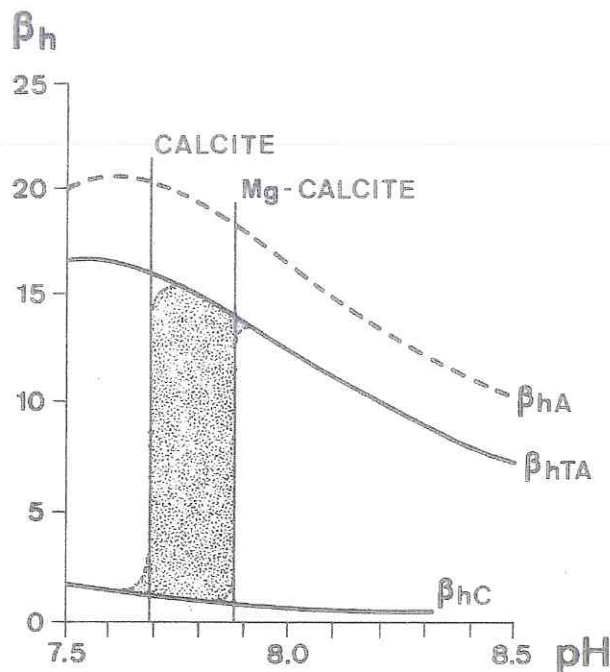


Fig.1 : Calculated homogenous buffer factors at constant carbonate concentration ( $\beta_{hc}$ ), at constant carbonate alkalinity ( $\beta_{hA}$ ) and at constant total alkalinity ( $\beta_{hTA}$ ) versus pH. Vertical lines indicate limits of solubility (20°C ; 38‰) of calcite and Mg-calcite (15% Mg).

It is possible to show theoretically (FRANKIGNOULLE, unpublished results) that the direction and intensity of the  $\text{CO}_2$  flux between ocean and atmosphere are related to the buffer factor. Preliminary experimental determinations of the flux and of the buffer factor confirm the validity of this rule in coastal mediterranean waters.

#### Experimental results

The air-sea  $\text{CO}_2$  exchanges have been measured in the Bay of Calvi (Corsica)

by IR spectroscopy using the plastic floating bell described by FRANKIGNOULLE and DISTECHE (1984). Since the total alkalinity keeps constant during the time range of the experiments (48 hours), the homogenous buffer factor  $\beta_{hTA}$  was calculated as described above. As shown on fig.2, the mean measured flux is linearly related to the calculated value of  $\beta_{hTA}$ .

We believe that by evaluating  $\beta_h$  for a given surface seawater, one can thus estimate and predict the direction and the magnitude of the  $CO_2$  flux at the interface. Fig.2 shows that influx (air $\rightarrow$ sea) can only occur for a buffer factor  $< 11$ . Mapping  $\beta_h$  values in surface waters corresponds to mapping regions as either sinks or sources of  $CO_2$ . Fig.3 shows that the Bay of Calvi is always emitting despite the intense photosynthetic activity of the Posidonia seagrass bed, except in the winter where it behaves as a weak sink for atmospheric  $CO_2$ .

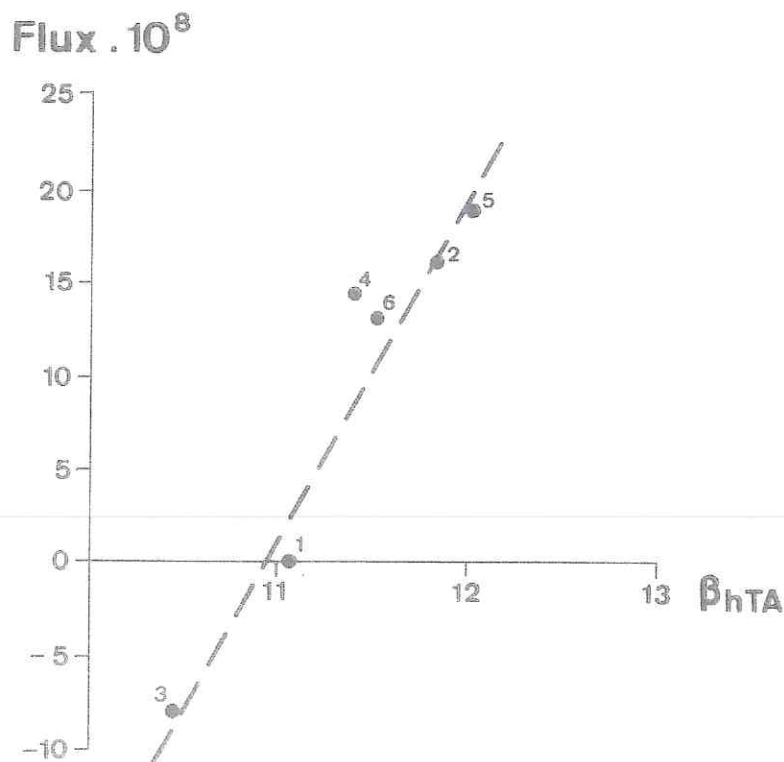


Fig.2 : Measured sea-air  $CO_2$  fluxes (flux  $> 0 \Rightarrow$  sea  $\rightarrow$  air) versus calculated homogenous buffer factor at constant total alkalinity. Fluxes are expressed in  $mM$  of  $CO_2/sec/m^2$ . (1=December 82 ; 2=September 83 ; 3=February 84 ; 4=March 84 ; 5=June 84 ; 6 = October 84).

It seems safe to say that the entire Posidonia belt present around the Mediterranean Sea, must behave in the same way and we are now trying to apply our methodology to other water types.

It can be shown that the  $\beta_h$  factor essentially depends on pH and only slightly changes with temperature, salinity and alkalinity. Accurate measure-



ments of pH are therefore, to our opinion, essential in evaluating and predicting the air-sea exchange of CO<sub>2</sub>.

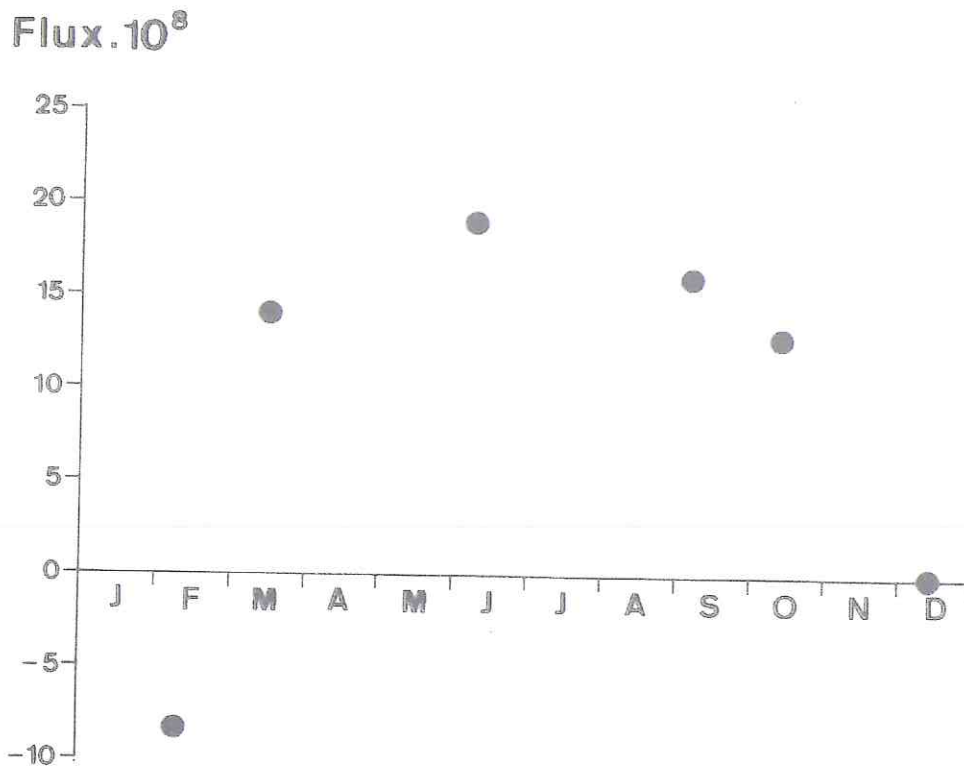


Fig.3 : Bay of Calvi. Annual variation of the measured air-sea CO<sub>2</sub> fluxes expressed in mM of CO<sub>2</sub>/sec/m<sup>2</sup>.

The pH of the water of our experimental site shows a yearly variation (fig.4)(FRANKIGNOULLE and DISTECHE, 1984). An acidity maximum is detected during the summer. During this period, one might reach conditions where the system goes over to a constant carbonate regime. We follow closely the annual cycle of the CO<sub>2</sub> system in this region for many years but have only hints that such conditions might actually prevail at the lowest pH values observed.

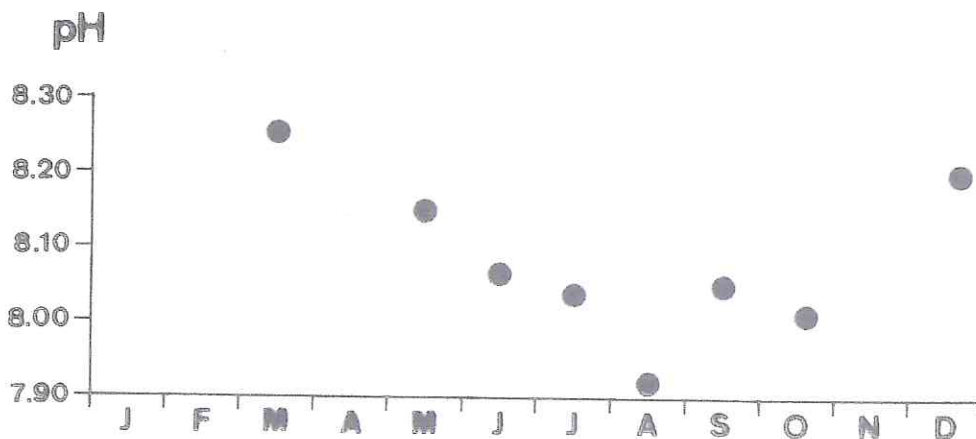


Fig.4 : Bay of Calvi. Annual variation of the measured pH (from FRANKIGNOULLE and DISTECHE, 1984).

## CONCLUSION

The determination of the homogenous buffer factor ( $\beta_h$ ) is useful in the study of CO<sub>2</sub> air-sea exchanges. It can be easily calculated for three thermodynamical constraints, respectively the constant carbonate, carbonate alkalinity and total alkalinity regimes. The choice of the constraint depends on the case study. In situ experimental results in Mediterranean coastal water show a good correlation between measured CO<sub>2</sub> fluxes and calculated buffer factor at constant total alkalinity. It seems thus possible to estimate the intensity and the direction of the flux from the properties of the surface seawater only, defined by a given  $\beta_h$  value. At lower pH (< 7.8) the transition to the carbonate constant regime might start to become dominant but in a still unknown way. Further investigations are needed especially on the solubility of magnesian calcites and the kinetics of their dissolution.

It is however promising to discover that it should be possible to map marine regions as sinks or sources of CO<sub>2</sub> only by carefully measuring their homogenous buffer factor and its annual variation. Monitoring the  $\beta_h$  factor at monthly intervals could become a very useful tool to survey how surface waters behave with respect to the atmospheric CO<sub>2</sub> level changes.

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