ECOHYDRODYNAMICAL STUDY OF THE LIGURO-PROVENCAL FRONT (CORSICAN AREA) : IV. SEA WATER CO₂ SYSTEM DATA.

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ABSTRACT

During three cruises in 1984, measurements of pH and alkalinity have been performed along a transect originating from Calvi to 30 miles off shore in order to describe the seawater CO₂ system in relation to the presence of the liguro-provençal front.

As total alkalinity does not change with photosynthesis or respiration, it can indicate water masses origin while CO₂ variations allow to estimate the biological activities.

This study reveals upwellings near the liguro-provençal front in March and June. Those upwellings allow high productivity at the surface level in March when no pycnocline can be detected and under the pycnocline in June.
INTRODUCTION

During March, June and October 1984, measurements of pH and alkalinity have been performed at ten selected stations along a transect originating from Calvi to 30 miles off shore (see HECQ et al., 1985) in order to describe the seawater CO₂ system in relation to the presence of the liguro-provençal front.

The seawater CO₂ system can be described after measurement of both pH and total alkalinity. The total alkalinity being independent of an input or an output of dissolved CO₂ (i.e. respiration and photosynthesis), it can be used to identify water masses as far as shell building or degradation are neglectable in the studied medium. On the other hand, the variations of the total inorganic carbon depends on biological processes. So, the seawater CO₂ system could appear to be very useful to study the water masses origin and inherent biological activity.

MATERIAL AND METHODS

Both parameters used in this study are total inorganic carbon (ΣCO₂) and total alkalinity (TA):

\[ \Sigma CO₂ = |CO₂| + |HCO₃^-| + |CO₃^{2-}| \]  \hspace{1cm} (1)
\[ TA = |HCO₃^-| + 2|CO₃^{2-}| + |B(OH)₄^-| \]  \hspace{1cm} (2)

where
\[ |CO₂| \] = concentration of dissolved CO₂
\[ |HCO₃^-| \] = concentration of bicarbonate
\[ |CO₃^{2-}| \] = concentration of carbonate
\[ |B(OH)₄^-| \] = concentration of borate

The water CO₂ chemistry can be described as follow :

\[ 2HCO₃^- \rightleftharpoons H₂O + CO₂ + CO₃^{2-} \]  \hspace{1cm} (3)

but also :
\[ H₃BO₃ + HCO₃^- \rightleftharpoons B(OH)₄^- + CO₂ \]  \hspace{1cm} (4)
Equations 3 and 4 show that an increase or a decrease of the dissolved \( \text{CO}_2 \) should not modify the total alkalinity since the base excess is conserved by both equilibria.

It means that TA should keep constant during respiration and/or photosynthesis process. Total alkalinity only varies by reactions involving carbonates exchanges (geochemical dissolution or precipitation, shell construction,...). BERNER et al. (1970) have discussed alkalinity changes in anoxic conditions.

A total inorganic carbon variation takes into account both alkalinity change and biological activity.

pH measurements have been performed by means of the pressure compensated electrochemical cell conceived by DISTECHE (1959,1962). The calibration is made with a phosphate buffer (FRANKIGNOLLE and DISTECHE, 1984). The error on the absolute pH value is 0.01 pH unit but we can detect 0.001 pH unit variation.

Vertical \textit{in situ} pH profiles are carried out to 70 meters depth.

The total alkalinity is measured by titration of the sample using the Gran's method (1952). The precision is 0.2%. Samplings are made at 1, 10, 20, 30, 40, 50, 60, 70, 80, 100, 150 and 200 meters.

\( \Sigma \text{CO}_2 \) (total inorganic carbon) is calculated using the method of MILLERO (1979), the dissociation constants for carbonic acid of MERBACH et al. (1973), the dissociation constant for boric acid of LYMAN (1957, cited by MILLERO, 1979) and the total borate concentration given by CULKIN (1965).

RESULTS AND DISCUSSION

Figures 1,2 and 3 show the variations of total alkalinity at four depths in March 84, June 84 and October 84.

In March 1984, a discontinuity – due to the front – characterizes stations \( \text{n}^\circ \) 3 and \( \text{n}^\circ \) 4. The alkalinity increases from the surface to the depth and from the coastal stations to the off shore ones. The highest values obtained at stations 4 and 5 could indicate the presence of an upwelling.
Fig. 1: Measured total alkalinity in March 84.

Fig. 2: Measured total alkalinity in June 84.
In June 84, a front has been also shown between stations n° 3 and n° 4. Deep and off shore waters are obviously more alkaline. There is an upwelling at station 7 up to 50 meters, which corresponds to the pycnocline (see HECQ et al., 1985).

Note that at station 10, at 40 meters depth, a high alkalinity value is found (TA = 2.711 meq.L⁻¹) correlated to high values of Chl A (GOFFART et al., 1985) and to high value of primary production (LICOT et al., 1985). This suggests the deep origin of alkaline nutriments-rich waters.

In October 1984, fig.3 reveals a better homogeneity of the water. The front stays at stations n° 5 (surface) and n° 4 (50 and 100 meters). No upwelling is suggested as in March and June.

![Graph showing TA concentration at different depths](image)

**Fig.3 :** Measured total alkalinity in October 84.

Figure 4 shows the calculated total inorganic carbon at four depths. To estimate the importance of photosynthesis and respiration processes, this figure must be compared to the total alkalinity one (fig.3). So, figure 4 reveals a minimum of $\Sigma$CO₂ at station 9 while alkalinity keeps constant and, on another hand, the maximum of the surface value of alkalinity at station 4 does not correspond to a change of the $\Sigma$CO₂. Moreover, the arithmetical difference between TA and $\Sigma$CO₂ is maximum for stations 9, 4 and 1. This means that the $\Sigma$CO₂ balance at those stations is negative showing that the photosynthesical processes are higher than respiratory ones. This result fits well with the measurements of the primary production described by LICOT et al. (1985).
Fig. 4: Calculated εCO₂ in October 84.

CONCLUSION

The total alkalinity is a tool to study the water masses origin. Deep waters of the Mediterranean Sea are more alkaline, their total alkalinity can indicate up- and downwellings.

Moreover, the total inorganic carbon - compared to the total alkalinity - allows to characterize the biological activity.

This study reveals upwellings near the liguro-provencal front in March and June. Those upwellings allow high productivity at the surface level in March when no pycnocline can be detected and under the pycnocline in June.

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