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Distribution of dissolved CO₂ in the Red Sea and correlations with other geochemical tracers

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ABSTRACT

The concentration of dissolved inorganic carbon in the Red Sea was studied using the following model:

$$\text{TCO}_2 = \text{TCO}_{2,0} + \Delta\text{TCO}_{2,\text{bio}} + \Delta\text{TCO}_{2,\text{ant}}.$$

The conservative part $\text{TCO}_{2,0}$ was correlated with the potential temperature T . The term $\Delta\text{TCO}_{2,\text{bio}}$ represents the exchanges with the marine biosphere and was expressed in the form $a\Delta X + b\Delta Y$ with $X = \text{O}_2, \text{NO}_3, \text{PO}_4$ and $Y = \text{TA}, \text{Ca}$. The term $\Delta\text{TCO}_{2,\text{ant}}$ represents the excess of TCO_2 due to the penetration of human induced CO_2 in the ocean, which was expressed in the form $co \exp(-(z - z_0)/H)$. As a result of the study, the contribution of each of the three identified signals was evaluated and the ratio C/O/N/P for the Red Sea basin was determined.

1. Introduction

Modelling the transport of dissolved CO₂ in the sea requires the knowledge both of the oceanic circulation and of the boundary conditions of the CO₂ system in the ocean. It is also important to take into account the production or consumption of dissolved CO₂ due to the exchanges with marine biosphere. In all these respects, tracers are particularly interesting tools since:

- conservative tracers which are in steady state in the ocean, such as temperature T and salinity S can be used to calculate the advective velocities and eddy diffusivities (Wunsch and Grant, 1982; Wunsch and Minster, 1982);
- tracers which are involved in the carbon cycle, such as total inorganic carbon TCO_2 , total alkalinity TA, oxygen O_2 , nitrate NO_3 , phosphate PO_4 and calcium Ca give informations on the CO₂-carbonate system in the ocean and on the exchanges between dissolved CO₂ and marine biosphere (Chen and Pytkowicz, 1979; Brewer, 1978; Chen, 1978; Bolin *et al.*, 1983);
- transient tracers which have been introduced recently into the ocean by human

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activities, such as carbon 14 (^{14}C) and tritium (^3H) resulting from nuclear explosions, or freons which are industrial gases with no natural sources can be used to estimate the anthropogenic CO_2 invasion in the ocean (Oeschger *et al.*, 1975; Siegenthaler, 1983; Broecker *et al.*, 1980; Weiss and Roether, 1980; Gammon *et al.*, 1982).

In this paper, we propose a method of systematic study of TCO_2 distribution in one region of the ocean versus the variations of other tracers which are either conservative or affected by the exchanges with marine biosphere.

The aim of this work is to point out the juxtaposition of three signals in any TCO_2 variation:

- the TCO_2 variation due to the mixing of water masses which is correlated with the variation of potential temperature T ;
- the TCO_2 variation due to the exchanges between dissolved CO_2 and marine biosphere which is correlated with the corresponding variations ΔO_2 , ΔTA , ΔNO_3 , ΔPO_4 and ΔCa of the other tracers involved in the carbon cycle; and
- the TCO_2 variation due to the penetration into the ocean of anthropogenic CO_2 which is identified in first approximation to the inverse of an exponential function of depth.

The calculation has been made from a set of data collected in the Red Sea in June and October 1982.

2. TCO_2 distribution in the ocean: a quantitative approach

The concentration of a sample of seawater in total inorganic carbon TCO_2 is:

$$\text{TCO}_2 = [\text{CO}_2]_{\text{dissolved}} + [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$$

since dissolved carbon dioxide in seawater is in equilibrium with carbonate and bicarbonate ions. TCO_2 variations in the ocean, either as a function of time t or of space coordinates (x, y, z) , are difficult to interpret directly because they are due to the combination of several processes. We have adopted the following model for this study:

$$\text{TCO}_2 = \text{TCO}_{20} + \Delta\text{TCO}_{2\text{bio}} + \Delta\text{TCO}_{2\text{ant}} \quad (1)$$

where TCO_{20} is the part of TCO_2 which is conservative and which is in a steady state; i.e., the value that TCO_2 would have in the absence of exchanges between dissolved CO_2 and the marine biosphere and in the absence of anthropogenic CO_2 in the ocean. TCO_{20} variations can be correlated with variations of the other conservative parameters of a water mass (Ben Yaakov, 1971), and in practice, we will look for a relation like: $\text{TCO}_{20} = f(T, S)$, where T is the potential temperature, S the salinity.

$\Delta\text{TCO}_{2\text{bio}}$ represents the production or consumption of TCO_2 through the

exchanges with marine biosphere. We can write:

$$\Delta\text{TCO}_2\text{bio} = \Delta\text{TCO}_2\text{org} + \Delta\text{TCO}_2\text{inorg}$$

where $\Delta\text{TCO}_2\text{org}$ is the production or consumption of TCO₂ through the exchanges with the organic carbon of the marine biosphere (photosynthesis, oxidation of organic matter), $\Delta\text{TCO}_2\text{inorg}$ is the production or consumption of TCO₂ through the exchanges with the inorganic carbon of the marine biosphere (biomineralization, redissolution of CaCO₃). Redfield *et al.* (1963) have related $\Delta\text{TCO}_2\text{org}$ with the corresponding variations of nitrogen, phosphorus, oxygen and alkalinity in the ratio 106/16/1/-138/-17.

In our study we shall put $\Delta\text{TCO}_2\text{org}/\Delta\text{N}/\Delta\text{P}/\Delta\text{O}/\Delta\text{A} = 106/\text{RN}/\text{RP}/\text{RO}/\text{RA}$. In the same way, we have $\Delta\text{TCO}_2\text{inorg}/\Delta\text{Ca}/\Delta\text{A} = 1/1/2$ where ΔCa is the production or consumption of calcium due to the exchanges with particulate CaCO₃. $\Delta\text{TCO}_2\text{bio}$ can be expressed in the form:

$$\Delta\text{TCO}_2\text{bio} = a\Delta X + b\Delta Y \quad (2)$$

where $\Delta X = \Delta\text{O}, \Delta\text{N}$ or ΔP and $\Delta Y = \Delta\text{A}$ or ΔCa .

$\Delta\text{TCO}_2\text{ant}$ represents the difference between the value of TCO₂ at the time t at a given place of the ocean and the pre-industrial value of TCO₂ at the same place; i.e., the TCO₂ variation due to the penetration of human induced CO₂ in the ocean. This variation is very small (0 to 2%) thus difficult to point out as the error on each measurement of TCO₂ is about 0.3%. At best one would like to be able to express $\Delta\text{TCO}_2\text{ant}$ in the form $\Delta\text{TCO}_2\text{ant} = cf(\Delta K)$ where ΔK is the concentration variation of an exclusively anthropogenic tracer (freon 11 or 12 for example). However, our data on such concentration variations is inadequate for the realization of this function; therefore, we have chosen to express $\Delta\text{TCO}_2\text{ant}$ as a function of depth:

$$\begin{aligned} \Delta\text{TCO}_2\text{ant} &= co && \text{for } Z < Z_0 \\ \Delta\text{TCO}_2\text{ant} &= co \exp(-(Z - Z_0)/H) && \text{for } Z \geq Z_0 \end{aligned} \quad (3)$$

where co represents the excess of TCO₂ in the mixed layer, Z_0 is the thickness of the mixed layer, H is a depth scale constant. The above relation means that the penetration of human induced CO₂ in the ocean is treated according to a one dimensional advective-diffusive model (Gammon *et al.*, 1982). From the expressions (1), (2) and (3) we have:

$$\begin{aligned} \text{TCO}_2 &= \text{TCO}_{20} + a\Delta X + b\Delta Y + co && \text{for } Z < Z_0 \\ \text{TCO}_2 &= \text{TCO}_{20} + a\Delta X + b\Delta Y + co \exp(-(Z - Z_0)/H) && \text{for } Z \geq Z_0 \end{aligned} \quad (4)$$

The data are treated in the following way:

In the mixed layer, which is an open system, the values of TCO₂₀, X_0 , Y_0 are

initially fixed by the conditions of equilibrium with the atmosphere and between the chemical species. In a first step, we seek to determine the functions:

$$\text{TCO}_2\text{o} = f(T, S)$$

$$X_o = g(T, S)$$

$$Y_o = h(T, S)$$

which best represent the correlation between TCO_2o , X_o , Y_o and the two main conservative parameters in water masses. To be exact, the first of these relations should be written:

$$\text{TCO}_2\text{o} + c_o = f(T, S)$$

since the present concentration of dissolved CO_2 in the mixed layer contains the signal of anthropogenic CO_2 .

In a second step, the parameters of relation (4) are determined using a least square fitting method which is a multilinear regression on the variables ΔX , ΔY and $\exp -(Z - Z_o)/H$ with adjusted values of Z_o and H to give the best fit of the data. Thus, we obtain the coefficients a and b of the relation (2) and the coefficients c_o , Z_o and H of the relation (3), so that the contribution of each "TCO₂ signal" can be evaluated. The choice of several combinations (X , Y) enables us to calculate the ratios RO, RN, RP, RA and to compare them with Redfield's values.

3. Merou data

The *Merou* cruise took place in two parts: from 16 June to 4 July 1982 and from 25 September to 9 October 1982. During each part of the cruise, a longitudinal section in the Red Sea was carried on, as well as five cross sections in the Strait of Bab el Mandab and several stations in the Gulf of Aden. Figure 1 shows the location of the stations. At each station, N samples of seawater were collected in the water column (N is approximately 25 for a depth of about 2000 m.) The data we have for one sample are:

- total alkalinity (TA) and total inorganic carbon (TCO_2) measured simultaneously by a potentiometric method derived from the one described by Dyrssen and Sillen (1967) and improved by Bradshaw and Brewer (1980), with an accuracy of respectively 0.1 and 0.3%;
- nutrients (nitrite NO_2 , nitrate NO_3 , silicate SiO_3 and phosphate PO_4) titrated on an automatic apparatus of the Technicon type according to the method recommended by Treguer and Le Corre (1975), with an accuracy of respectively 1, 0.3, 0.3 and 0.5%;
- oxygen (O_2) titrated by the Winkler method (Carpenter, 1965), with an accuracy of 1%;
- calcium (Ca) and magnesium (Mg) titrated by a complexometric method with an accuracy of 0.2% (Lebel and Poisson, 1976);

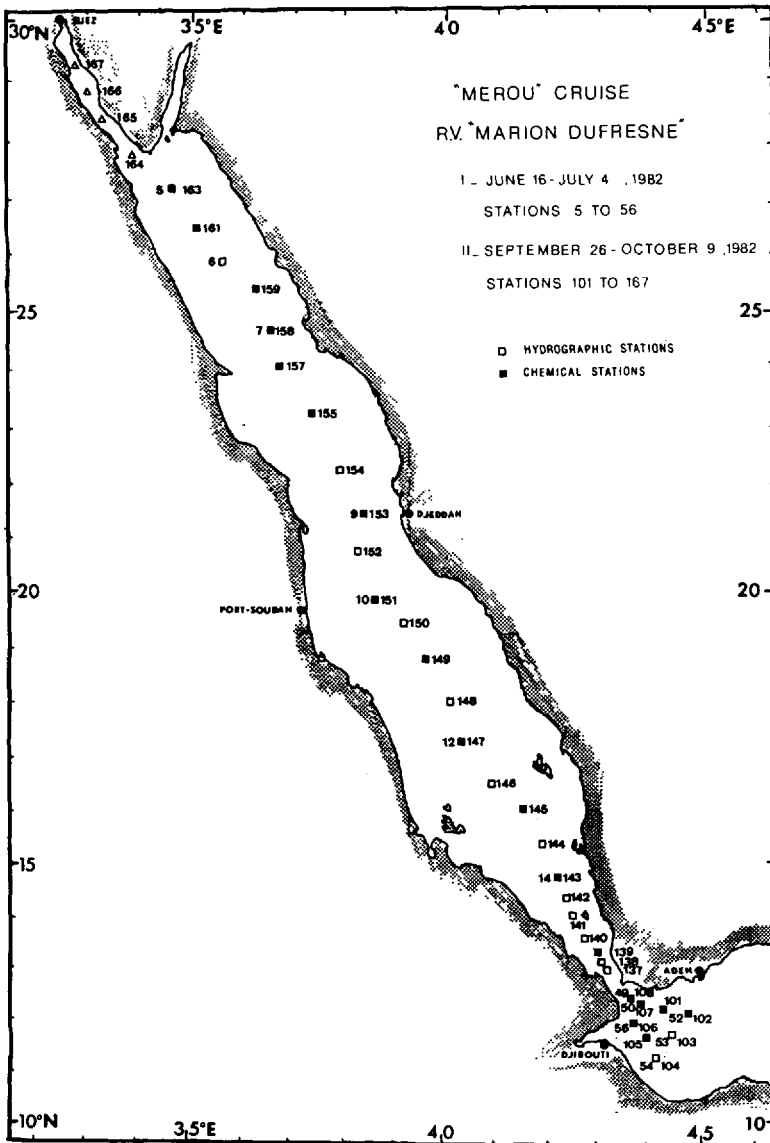


Figure 1. Chemical and hydrographic stations of the *Merou* cruise (1982) in the Red Sea.

- temperature (T_e) interpolated from CTD profiles with an accuracy of 0.005°C; and
- salinity (S) measured with a Guidline autosal salinometer with an accuracy of 0.002.

Other measurements made during the *Merou* cruise are not mentioned here because they are not taken into account in this study. Figure 2 shows the distribution of the data

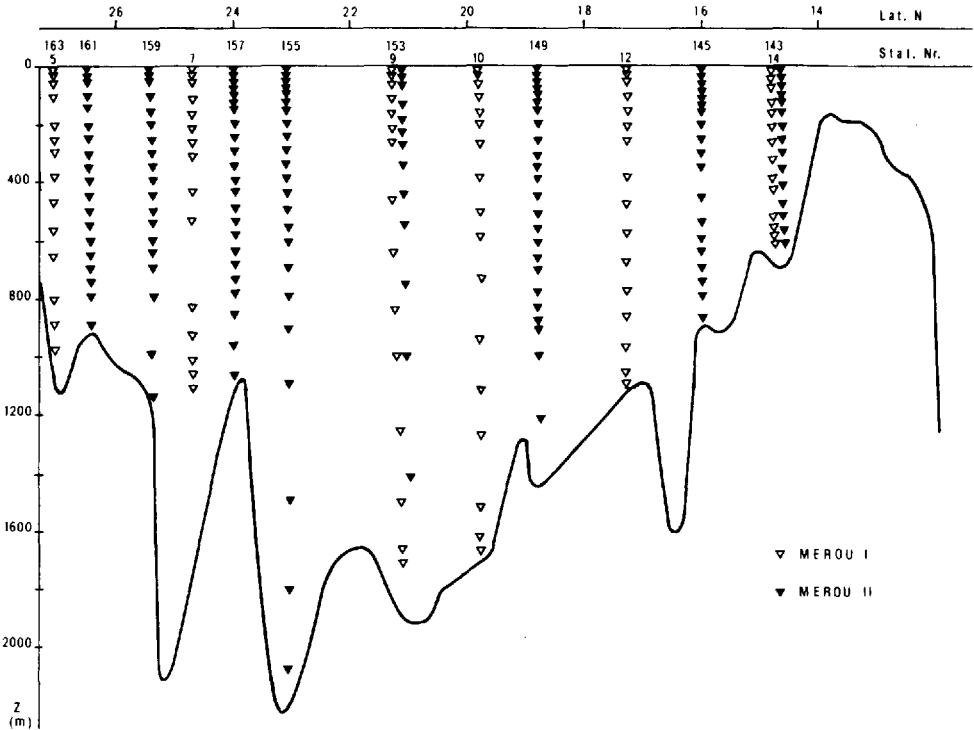


Figure 2. Distribution of data with latitude and depth.

as a function of latitude and depth. The concentration of the different chemical species is expressed in $\mu\text{mole/kg}$ of seawater. The potential temperature T used in the calculations is deduced from the *in-situ* temperature T_e (Fofonoff and Millard, 1980). The salinity used is the practical salinity 1978 (Unesco, 1981). The data for one station, which gives an example of the values of the different parameters, are shown in Table 1.

4. Results

We sought to establish the correlation between the conservative parts of each chemical species Q involved in the carbon cycle ($Q = \text{TCO}_2, \text{TA}, \text{O}_2, \text{NO}_3, \text{PO}_4, \text{Ca}$) and the potential temperature T and salinity S . We expected this correlation to be linear in the following form:

$$Q_0 = A + BT + CS$$

where A, B, C are constants, one or more of which might possibly be equal to zero. The

Table 1. Data for station 155 of *Merou II* cruise. Potential temperature is in °C, *S* is the practical salinity, TA is in meq/kg, TCO₂ is in mmole/kg, NO₂, NO₃, PO₄, SiO₃ and O₂ are in μmole/kg, Ca is in g/kg.

| Station 155 | | | | | | | | | | |
|-------------|-------|--------|-------|------------------|------|-----------------|-----------------|-----------------|------------------|----------------|
| Z | POT.T | S | TA | TCO ₂ | Ca | NO ₂ | NO ₃ | PO ₄ | SiO ₃ | O ₂ |
| 0 | 29.44 | 39.699 | 2.421 | 2.019 | .471 | .30 | .15 | .07 | .00 | 201 |
| 10 | 29.41 | 39.699 | 2.439 | 2.030 | .472 | .30 | .15 | .12 | .00 | 199 |
| 20 | 29.31 | 39.699 | 2.449 | 2.036 | .472 | .30 | .15 | .10 | .00 | 200 |
| 35 | 28.54 | 39.594 | 2.432 | 2.025 | .470 | .30 | .15 | .10 | .00 | 224 |
| 50 | 24.76 | 39.549 | 2.434 | 2.037 | .470 | .30 | .15 | .10 | .00 | 229 |
| 75 | 24.48 | 39.579 | 2.445 | 2.054 | .471 | .30 | .15 | .23 | .00 | 213 |
| 100 | 24.23 | 39.589 | 2.436 | 2.059 | .472 | .30 | .15 | .18 | .00 | 203 |
| 125 | 23.96 | 39.886 | 2.427 | 2.065 | .474 | .30 | 1.95 | .25 | .20 | 186 |
| 150 | 23.37 | 39.884 | 2.431 | 2.070 | .476 | .30 | 2.70 | .25 | .25 | 183 |
| 200 | 22.06 | 40.377 | 2.439 | 2.080 | .480 | .30 | 3.60 | .35 | .60 | 183 |
| 250 | 21.98 | 40.395 | 2.449 | 2.102 | .479 | .30 | 5.70 | .31 | 1.50 | 170 |
| 300 | 21.75 | 40.468 | 2.447 | 2.141 | .481 | .30 | 12.15 | .70 | 5.60 | 111 |
| 350 | 21.67 | 40.525 | 2.432 | 2.161 | .483 | .30 | 16.20 | .90 | 8.65 | 79 |
| 392 | 21.64 | 40.546 | 2.427 | 2.175 | .481 | .30 | 17.85 | .96 | 11.15 | 57 |
| 442 | 21.63 | 40.561 | 2.433 | 2.175 | .482 | .30 | 18.75 | .98 | 12.10 | 54 |
| 492 | 21.62 | 40.570 | 2.433 | 2.176 | .482 | .30 | 18.90 | .95 | 12.65 | 51 |
| 543 | 21.61 | 40.575 | 2.432 | 2.175 | .483 | .30 | 18.60 | 1.00 | 12.65 | 52 |
| 593 | 21.60 | 40.577 | 2.428 | 2.168 | .483 | .30 | 17.70 | .97 | 12.10 | 63 |
| 693 | 21.58 | 40.581 | 2.428 | 2.159 | .481 | .30 | 17.10 | .90 | 12.10 | 70 |
| 794 | 21.56 | 40.584 | 2.437 | 2.158 | .482 | .30 | 16.20 | .86 | 11.50 | 79 |
| 894 | 21.55 | 40.583 | 2.423 | 2.142 | .483 | .30 | 15.00 | .82 | 10.95 | 88 |
| 995 | 21.53 | 40.585 | 2.433 | 2.146 | .483 | .30 | 13.95 | .77 | 9.90 | 97 |
| 1196 | 21.52 | 40.582 | 2.447 | 2.146 | .479 | .30 | 13.20 | .72 | 8.85 | 102 |
| 1497 | 21.51 | 40.576 | 2.441 | 2.146 | .484 | .30 | 13.20 | .70 | 8.85 | 104 |
| 1799 | 21.51 | 40.582 | 2.442 | 2.143 | .483 | .30 | 13.20 | .70 | 8.85 | 105 |
| 2100 | 21.51 | 40.581 | 2.442 | 2.143 | .484 | .30 | 12.45 | .71 | 8.85 | 108 |

choice of a linear correlation with *T* and *S* appears to be justified for the following reasons:

- for a marine basin where *n* masses of water are mixed, any conservative quantity can theoretically be expressed as a function of (*n* - 1) other conservative parameters (Ben Yaakov, 1971), and
- the hydrology of the Red Sea is relatively simple. For instance, the *TS* diagram for all the stations in June (which is the end of the winter period when the deep water has formed in the north of the Red Sea) shows that each sample of seawater can be considered as resulting from the mixing of at the most three masses of water (see Fig. 3).

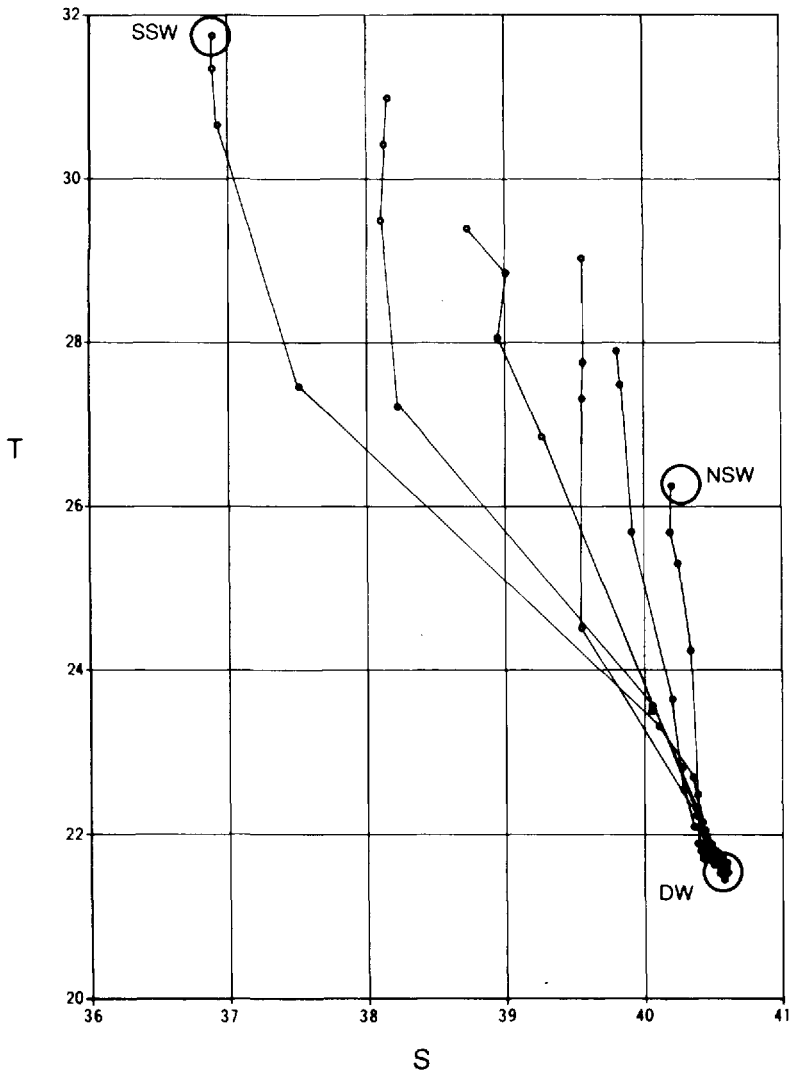


Figure 3. *TS* curves for the *Merou I* cruise (stations 5 to 14).

For each chemical species Q , we considered several possibilities:

$$Q_0 = A + BT$$

$$Q_0 = A + CS$$

$$Q_0 = A + BT + CS$$

$$Q_{0.35} = A + BT$$

Table 2. Correlation $Q = f(T, S)$ in the surface layer for the chemical species $Q = \text{TCO}_2$, TA, O₂, NO₃, PO₄ and Ca. T is the potential temperature in °C, S is the practical salinity. The numbers in parentheses are the standard deviations of the least squares fit for the above equations. For each tracer, the relation which best represents the data is underlined.

| | $Q = A + BT$ | $Q = A + CS$ | $Q = A + BT + CS$ | $Q_{35} = A + BT$ |
|------------------|-----------------------|-----------------------|----------------------------|-------------------|
| TCO ₂ | <u>2400 - 13T</u> | 1385 + 16S | 1940 - 7.9T + 8.0S | 2247 - 12T |
| μeq/kg | (16) | (19) | (18) | (48) |
| TA | 2338 + 2.12T | 1425 + 26S | <u>1345 + 2.3T + 26.5S</u> | 2161 + 3.26T |
| μeq/kg | (28) | (9) | (6) | (53) |
| O ₂ | <u>253 - 2T</u> | 96 + 2.54S | 189 - 1.19T + 1.05S | 154 + 0.98T |
| μmole/kg | (6) | (9) | (9) | (11) |
| NO ₃ | <u>0.25 + 0.011T</u> | 1.01 - 0.011S | 0.75 + 0.006T + 0.007S | 0.06 + 0.008T |
| μmole/kg | (.14) | (.15) | (.19) | (.35) |
| PO ₄ | <u>-0.08 + 0.009T</u> | 0.70 - 0.014S | 0.35 + 0.004T - 0.007S | 0.30 + 0.007T |
| μmole/kg | (.11) | (.12) | (.15) | (.32) |
| Ca | 13590 - 67.3T | <u>124.7 + 299.4S</u> | 2994 - 94.8T + 349.3S | 10578 - 6.4T |
| μmole/kg | (449) | (175) | (349) | (324) |

where $Q_{0.35}$ is the value of the quantity Q standardized for a salinity of 35, that is $Q_{0.35} = (Q_{0S}/S) \times 35$.

This latter possibility is not a strictly linear relationship with T and S but, for completeness, we examined it since it has been used in other investigations (Brewer, 1978). Table 2 gives the values for the constants A , B , C in the above formulas obtained by linear regression of the quantity Q as a function of T and S for all the surface data. For each chemical species, we selected the relationship which best represented the data, that is which corresponded to the smallest standard error. The results thus obtained are underlined in Table 2.

The coefficients a , b , co , Z_0 and H are then calculated from:

$$\text{TCO}_2 = \text{TCO}_{20} + a\Delta X + b\Delta Y + co \exp -(Z - Z_0)/H$$

and

$$\text{TCO}_{20} = f(T, S) - co$$

that is:

$$\text{TCO}_2 = f(T, S) + a\Delta X + b\Delta Y + co \exp -(Z - Z_0)/H - co.$$

A least square fit of all the summer data give for $X = 0$ and $Y = \text{TA}$ the coefficients:

$$a = -0.79(\pm 0.015)$$

$$b = 0.64(\pm 0.15)$$

$$co = 55(\pm 5) \mu\text{mole/kg}$$

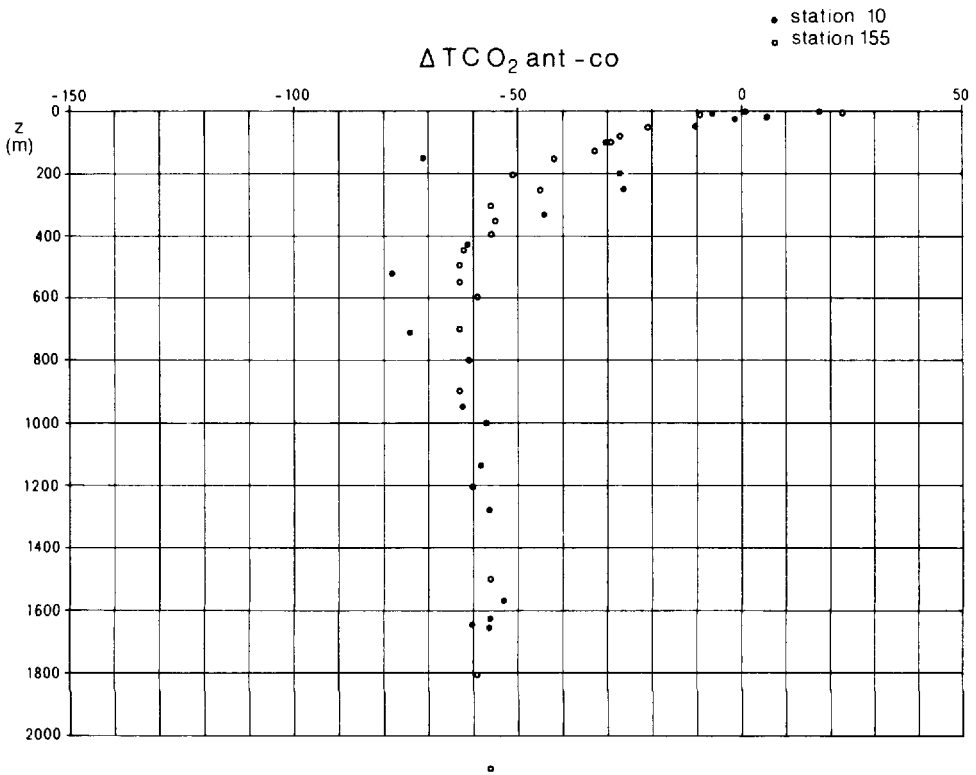


Figure 4. Variations of $(\Delta\text{TCO}_2^{\text{ant}} - co)$ with depth for the stations 10 (*Merou I*) and 155 (*Merou II*).

$$Z_0 = 30(\pm 5) \text{ m}$$

$$H = 100(\pm 30) \text{ m}$$

Figure 4 shows the variations with depth of $\Delta\text{TCO}_2^{\text{ant}}$ estimated from the data of two different stations by calculating the left-hand term of:

$$\text{TCO}_2 - f(T, S) - a\Delta X - b\Delta Y = co \exp -(Z - Z_0)/H - co.$$

The same calculation has been made for all the summer data and the set of values obtained is compared in Figure 5 with the theoretical curve $\Delta\text{TCO}_2^{\text{ant}} - co = F(Z) = 55 \exp -(Z - 30)/100 - 55$. These results show that $\Delta\text{TCO}_2^{\text{ant}}$ can be calculated using the above expression with an average error of $\pm 14 \mu\text{mole/kg}$.

The coefficients a and b obtained successively for $X = \text{O}_2, \text{NO}_3, \text{PO}_4$ and $Y = \text{TA}, \text{Ca}$ are indicated in Table 3, together with the theoretical values for a and b expressed as a function of RO, RN, RP and RA.

The results show that the variation $\Delta\text{TCO}_2^{\text{org}}$ of the concentration of TCO_2 due to

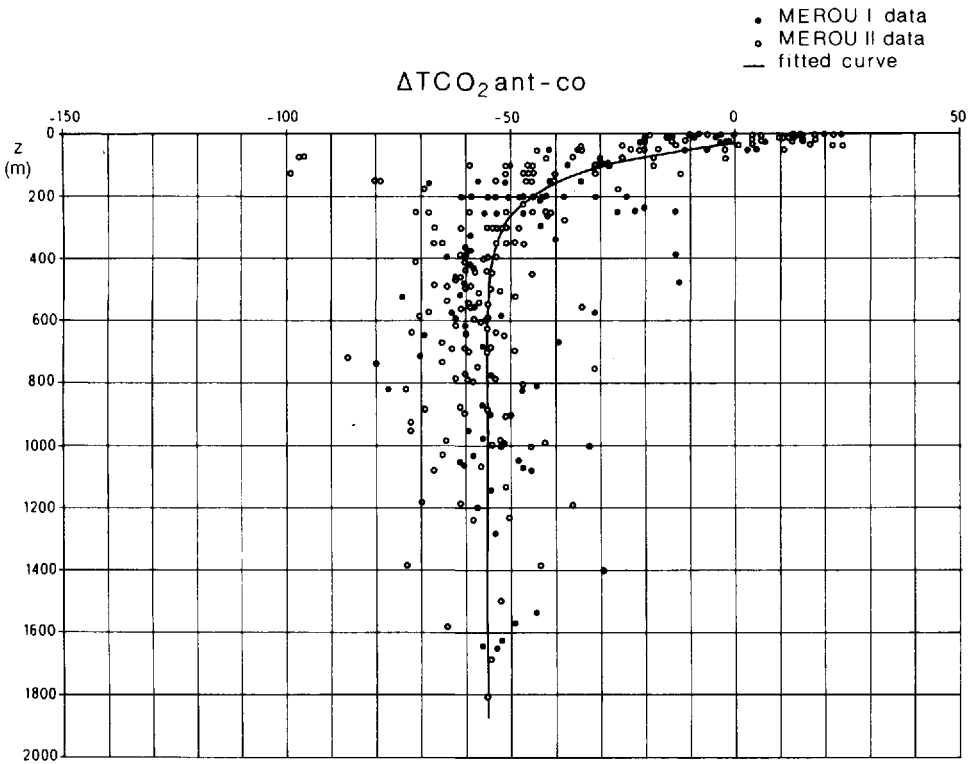


Figure 5. Comparison of all the calculated values of $(\Delta\text{TCO}_2\text{ant} - \text{co})$ with the fitted function $(\text{co} \exp(-(z - z_0)/H) - \text{co})$.

Table 3. Values of a and b in the relation $\text{TCO}_2 = \text{TCO}_2\text{o} + a(X - X_0) + b(Y - Y_0) + \text{co} \exp(-(z - z_0)/H)$ obtained for $X = \text{O}_2, \text{NO}_3, \text{PO}_4$ and for $Y = \text{TA}, \text{Ca}$.

| (X, Y) | a | b | Theoretical value of a | Theoretical value of b |
|----------------------------|---------------------|---------------------|---|--------------------------|
| (O_2, TA) | $-0.79 (\pm 0.015)$ | $0.64 (\pm 0.15)$ | $\frac{106}{\text{RO}} \left(1 - 0.50 \frac{\text{RA}}{106}\right)$ | 0.50 |
| (NO_3, TA) | $7.70 (\pm 0.15)$ | $0.52 (\pm 0.15)$ | $\frac{106}{\text{RN}} \left(1 - 0.50 \frac{\text{RA}}{106}\right)$ | 0.50 |
| (PO_4, TA) | $124 (\pm 3)$ | $0.38 (\pm 0.15)$ | $\frac{106}{\text{RP}} \left(1 - 0.50 \frac{\text{RA}}{106}\right)$ | 0.50 |
| (O_2, Ca) | $-0.78 (\pm 0.015)$ | $0.056 (\pm 0.050)$ | $106/\text{RO} = \Delta\text{C}/\Delta\text{O}_2$ | 1 |
| (NO_3, Ca) | $7.55 (\pm 0.15)$ | $0.071 (\pm 0.050)$ | $106/\text{RN} = \Delta\text{C}/\Delta\text{NO}_3$ | 1 |
| (PO_4, Ca) | $121 (\pm 3)$ | $0.038 (\pm 0.050)$ | $106/\text{RP} = \Delta\text{C}/\Delta\text{PO}_4$ | 1 |

the exchanges with the organic carbon of the marine biosphere is correlated effectively with the variations ΔO_2 , ΔNO_3 , ΔPO_4 . The values obtained for the a coefficient have a precision of $\pm 2\%$.

Concerning the variation $\Delta\text{TCO}_2\text{inorg}$, the correlation with ΔTA is compatible with the hypothesis $\Delta\text{TCO}_2\text{inorg}/\Delta\text{TA} = 1/2$ but the precision with respect to b is poor:

$$b = 0.50(\pm 0.15).$$

Finally, the correlation between $\Delta\text{TCO}_2\text{inorg}$ and ΔCa is very weak and cannot be used to support the hypothesis $\Delta\text{TCO}_2\text{inorg}/\Delta\text{Ca} = 1/1$. Specifically, the variations ΔTA for all the data are of the order of $\pm 60 \mu\text{mole/kg}$ which corresponds to a $\Delta\text{TCO}_2\text{inorg}$ signal of the order of $\pm 30 \mu\text{mole/kg}$. However, the experimental error of 0.2% on Ca corresponds to $\pm 50 \mu\text{mole/kg}$, hence any signal in $\Delta\text{TCO}_2\text{inorg}/\Delta\text{Ca}$ is lost. The values obtained from the data of Table 3 give for RO, RN and RP:

$$106/\text{RO} = -0.780(\pm 0.015)$$

$$106/\text{RN} = 7.70(\pm 0.15)$$

$$106/\text{RP} = 121(\pm 3)$$

That is the ratio C/O/N/P for the whole Red Sea basin equal to $106/-136/14/0.9$

The lack of precision for the b coefficient prevents the calculation of RA by comparing the values of a for the pair (X, TA) and for the pair (X, Ca), which would give:

$$\frac{a(X, \text{TA})}{a(X, \text{Ca})} = \left(1 - 0.50 \frac{\text{RA}}{106}\right).$$

If we suppose $\text{RA} = -17$, the ratio $a(X, \text{TA})/a(X, \text{Ca})$ is approximately 1.08. According to our results it is of the order of 1.02. This does not therefore allow RA to be calculated with sufficient precision, because the error on the coefficients $a(X, \text{TA})$ and $a(X, \text{Ca})$ is of the order of 2% . The ratio C/O/N/P thus calculated shows that in the Red Sea basin, the value of the ratio C/O is very close to Redfield's value. The ratios C/N and C/P are however greater than Redfield's values, which reflects a smaller proportion of nutrients relative to carbon in the organic matter.

5. Discussion

The aim of this study was to correlate the TCO_2 variations in the Red Sea with those of the other geochemical tracers. By using the following model:

$$\text{TCO}_2 = \text{TCO}_{20} + \Delta\text{TCO}_{2\text{bio}} + \Delta\text{TCO}_{2\text{ant}}$$

we have obtained the relations that permit us to calculate TCO_{20} , $\Delta\text{TCO}_{2\text{bio}}$ and

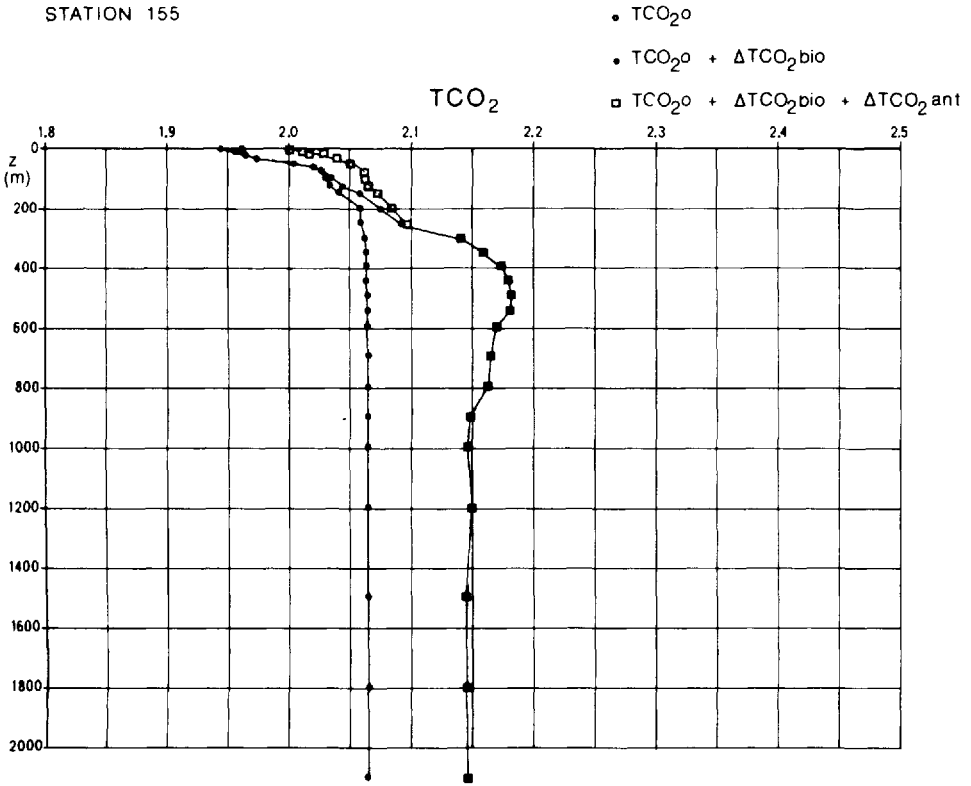


Figure 6. Contribution of TCO_{2o}, ΔTCO_{2bio} and ΔTCO_{2ant} to the calculated value of TCO₂.

ΔTCO_{2ant} as functions of measurements made on the seawater sample:

$$TCO_{2o} = (2400 - 13T) - 55 \tag{5}$$

$$\Delta TCO_{2bio} = -0.79(O_2 - O_{2o}) + 0.50(TA - TAo) \tag{6}$$

$$\Delta TCO_{2ant} = 55 \exp(-(z - 30)/100) \tag{7}$$

$$O_{2o} = 253 - 2T \tag{8}$$

$$TAo = 1345 + 2.3T + 26.5S. \tag{9}$$

Figure 6 represents the respective contributions of the signals TCO_{2o}, ΔTCO_{2bio} and ΔTCO_{2ant} at the value of TCO₂ calculated from relations (5) to (9). Figure 7 represents the difference between the measured and the calculated value of TCO₂ for station 155. On the whole set of *Merou I* and *Merou II* data, the standard deviation on TCO₂ calculated from the relations (5) to (9) is ±15 μmole/kg; i.e., 2.5 times higher than experimental error.

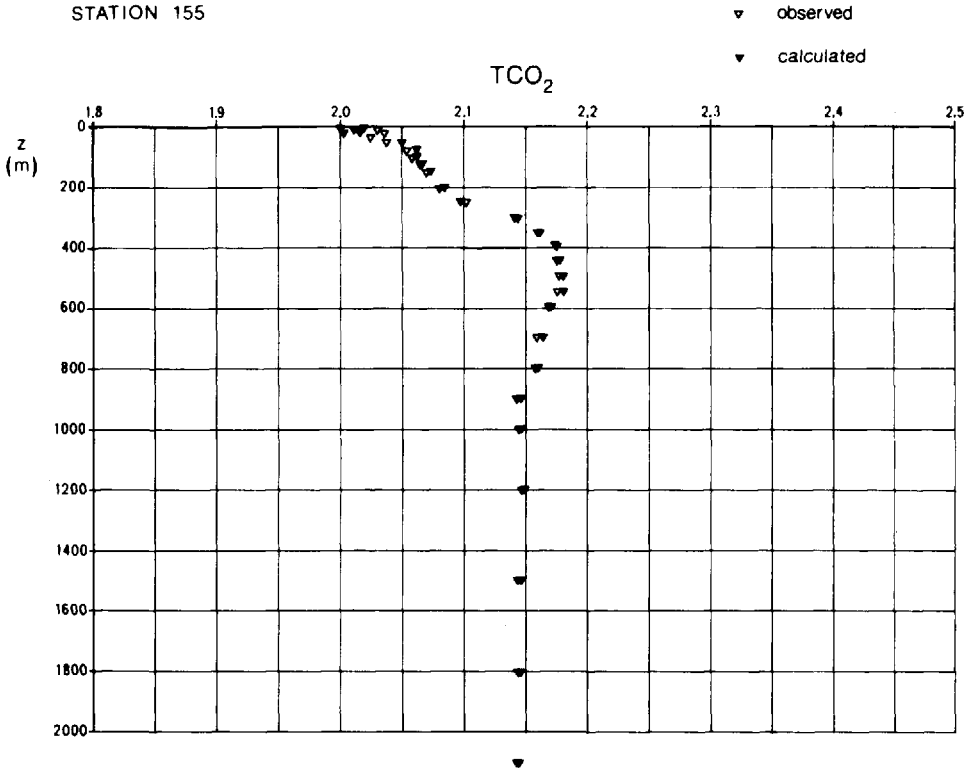


Figure 7. Comparison between TCO₂ measured and TCO₂ calculated for the station 155.

To obtain this result, a number of assumptions were made which are as follows:

- the conservative part Q_o of each tracer Q can be correlated to the value of the parameter Q in the mixed layer;
- the relation $Q_o = f(T, S)$ determined from the data of the mixed layer remains the same in deeper waters;
- the excess of anthropogenic CO₂ can be estimated by calculating the signal of a conservative tracer using a vertical advective-diffusive model; and
- the only processes which produce variations in the concentrations of O₂, NO₃, PO₄, TA, and Ca (apart from the mixing of water masses) are the exchanges between dissolved CO₂ and organic or inorganic carbon of the marine biosphere.

Another method of calculation, the multilinear regression analysis (Ben Yaakov, 1971), would provide correlates of the TCO₂ variations with those of the other geochemical tracers. For example, we obtain:

$$\text{TCO}_2 = A_0 + A_1T + A_2\text{O}_2 + A_3\text{TA} \quad (10)$$

with the regression of the measured values of TCO₂ as a function of T, O₂ and TA. This method has the advantage that no assumption is made on the different tracers and their variations. We have not chosen it, however, for the main part of this study for several reasons:

- the shift of the coefficients A_0, A_1, A_2, A_3 is very important from one station to another, and between the set of *Merou I* data and the set of *Merou II* data, hence a lack of accuracy on the ratios RO, RN, and RP;
- the relation (10) does not permit an estimate of the $\Delta\text{TCO}_2\text{bio}$ term, since all the conservative quantities (O_{2o}, TaO, TCO_{2o}) are included in the expression $A_0 + A_1T$; and
- the $\Delta\text{TCO}_2\text{ant}$ term cannot be evaluated by this type of calculation, since the errors on the different terms A_0, A_1T, A_2O_2 , and $A_3\text{TA}$ are much greater than the signal $\Delta\text{TCO}_2\text{ant}$.

Yet, the study of the data by multilinear regression analysis enables us to confirm part of the assumptions made for our study. Consequently, we have used it for the discussion of the results. Table 4 permits us to compare the linear relations:

$$\begin{aligned} \text{TCO}_2 &= f(T, X, \text{TA}) & \text{for } X = \text{O}_2, \text{NO}_3, \text{PO}_4 \\ \text{O}_2 &= f(T, X) & \text{for } X = \text{NO}_3, \text{PO}_4 \end{aligned}$$

obtained from our calculations, and those obtained using multilinear regression analysis on the set of data. This comparison shows that:

- our results are compatible with the multilinear regression analysis;
- the regressions $\text{TCO}_2 = f(T, X, \text{TA})$ are not accurate enough as regards the coefficients of X and TA to determine the ratios RO, RN, and RP; the result is particularly bad for $X = \text{NO}_3$ and $X = \text{PO}_4$; and
- the regressions $\text{O}_2 = f(T, \text{NO}_3)$ and $\text{O}_2 = f(T, \text{PO}_4)$ give accurate results; the values of the ratios O/N and O/P thus determined are in good agreement with our calculations.

Besides, an interesting point is that the conservative part of O₂ which can be found in the regression:

$$\begin{aligned} \text{O}_2 &= \text{O}_{2o} + \frac{\text{RO}}{\text{RN}} (\text{NO}_3 - \text{NO}_{3o}) \\ &= \text{O}_{2o} - \frac{\text{RO}}{\text{RN}} \text{NO}_{3o} + \frac{\text{RO}}{\text{RN}} \text{NO}_3 \end{aligned}$$

is close to O_{2o} ($\text{RO}/\text{RN} \text{NO}_{3o} \ll \text{O}_{2o}$). Thus the linear regression $\text{O}_2 = f(T, \text{NO}_3)$ enables us to confirm the expression of O_{2o} that was given in Table 2, i.e.:

$$254 - 2.05T \approx 253 - 2T$$

Table 4. Comparison of linear relations between tracers obtained from our results (Tables 2 and 3) with multivariable regression analysis.

| Relation | Calculated from Tables 2 and 3 | Multivariable Regression |
|---|--|---|
| $\text{TCO}_2 = f(T, \text{O}_2, \text{TA})$ | $1347(\pm 50) - 15(\pm 0.5)T - 0.79(\pm 0.015)\text{O}_2 + 0.5(\pm 0.15)\text{TA}$ | $1426(\pm 140) - 17(\pm 3)T - 0.74(\pm 0.05)\text{O}_2 + 0.49(\pm 0.22)\text{TA}$ |
| $\text{TCO}_2 = f(T, \text{NO}_3, \text{TA})$ | $1152(\pm 50) - 12(\pm 0.5)T - 7.7(\pm 0.15)\text{NO}_3 + 0.5(\pm 0.15)\text{TA}$ | $1729(\pm 300) - 13(\pm 3)T - 5.9(\pm 2.4)\text{NO}_3 + 0.20(\pm 0.35)\text{TA}$ |
| $\text{TCO}_2 = f(T, \text{PO}_4, \text{TA})$ | $1164(\pm 50) - 13(\pm 0.5)T - 124(\pm 3)\text{PO}_4 + 0.5(\pm 0.15)\text{TA}$ | $2190(\pm 1000) - 14(\pm 3)T - 48(\pm 40)\text{PO}_4 + 0.14(\pm 0.40)\text{TA}$ |
| $\text{O}_2 = f(T, \text{NO}_3)$ | $255(\pm 5) - 2.10(\pm 0.05)T - 9.68(\pm 0.30)\text{NO}_3$ | $254(\pm 5) - 2.05(\pm 0.10)T - 9.30(\pm 0.35)\text{NO}_3$ |
| $\text{O}_2 = f(T, \text{PO}_4)$ | $241(\pm 5) - 0.605(\pm 0.05)T - 155(\pm 5)\text{PO}_4$ | $247(\pm 5) - 0.662(\pm 0.15)T - 162(\pm 10)\text{PO}_4$ |

which justifies the assumptions made on the conservative part of O_2 . To sum up, our method presents the inconvenience, relative to multilinear regression analysis, of requiring numerous assumptions. However the results are more accurate as regards the expression $TCO_2 = f(T, O_2, TA)$ and permit us to determine the ratio C/O/N/P. The ratio O/N/P obtained with our procedure is in agreement with the results of the linear regressions $O_2 = f(T, NO_3)$ and $O_2 = f(T, PO_4)$.

6. Conclusion

We have been able to point out the superposition of three signals in the variations of TCO_2 . (1) The conservative part which is in a steady state ($TCO_{2,0}$) could be expressed as a function of potential temperature T . (2) The variation $\Delta TCO_{2,bio}$ due to the exchanges between dissolved CO_2 and marine biosphere has been correlated for the organic fraction with the variations ΔO_2 , ΔNO_3 and ΔPO_4 of the other tracers involved in the organic carbon cycle. The inorganic fraction of $\Delta TCO_{2,bio}$ due to the exchanges between the particulate $CaCO_3$ and the dissolved CO_2 could not be correlated in a satisfactory way to the variations of dissolved Ca, and the correlation with the variations of TA was compatible with the theoretical value of 0.50, but not very accurate. (3) The $\Delta TCO_{2,ant}$ signal due to the penetration of human induced CO_2 into the ocean has been described by the function $55 \exp -(Z - 30)/100$ with an averaged error of $\pm 14 \mu\text{mole/kg}$. Finally, the ratio C/O/N/P determined for the Red Sea are 106/-136/14/0.9, and a portion of this result, namely for the ratio O/N/P, is consistent with a multilinear regression analysis of the data.

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