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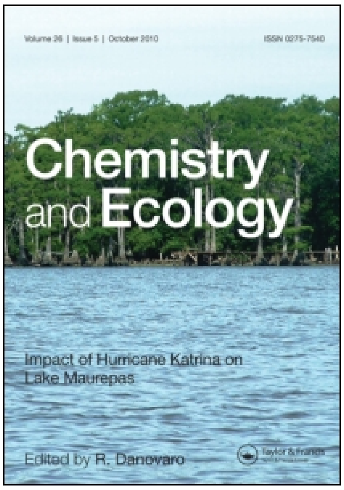

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Carbon dioxide chemistry of the SE Mediterranean open waters off Egypt

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Carbon dioxide chemistry of the SE Mediterranean open waters off Egypt

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The research cruise was conducted on board the R/V Meteor M51/2 during October–November 2001. Four deep stations located north of Rosetta branch of the River Nile (st. 546), Dabaa (st. 547) and Salloom (sts. 549 and 550) were selected to represent CO_2 components in the SE Mediterranean open waters off Egypt. Total alkalinity, salinity, temperature and pH were measured. Bicarbonate, partial pressure, dissolved and total CO_2 were calculated. The study area was divided into four water masses: SW, LIW, MDW and DW masses. MDW mass showed, on average, the highest concentrations of total alkalinity (1.99 ± 0.63 meq l^{-1}), bicarbonate (1.77 ± 0.49 mM l^{-1}), total CO_2 (1.75 ± 0.54 mM l^{-1}), P_{CO_2} ($0.34 \pm 0.21 \times 10^{-3}$ atmosphere) and D_{CO_2} (13.55 ± 8.31 mM l^{-1}). These high concentrations were due to the fact that most organic debris produced in the SW and LTW was destroyed in MDW and recycled there. All investigated parameters, on average, showed the lowest values of pH (8.20 ± 0.04), total alkalinity (1.52 ± 0.86 meq l^{-1}), bicarbonate (1.42 ± 0.85 mM l^{-1}), total CO_2 (1.30 ± 0.77 mM l^{-1}), P_{CO_2} ($0.18 \pm 0.09 \times 10^{-3}$ atmosphere) and dissolved CO_2 (7.08 ± 3.79 mM l^{-1}) in the DW. These low values may be due to the fact that within the DW reservoir CO_2 can be utilized in the dissolution of sedimentary carbonates.

Keywords: Carbon dioxide; Total alkalinity; pH; SE Mediterranean; Egypt

1. Introduction

Atmosphere is considered the major source of gases dissolved in seawater, due to its composition of a mixture of major, minor and trace gases. The marine environment can be considered as either a source or a sink for atmospheric gases, as gases enter or leave the marine environment via exchange across the air sea interface, and are transported within the sea water reservoir by physical and biological processes [1, 2].

During their residence in the sea, some gases behave in a conservative manner. In contrast, other gases are reactive and take part in biological and chemical processes. Dissolved gases are important for a number of reasons, but from the point of view of marine geochemistry, most significant implications of their presence in sea water are related to the role they play in the oceanic biogeochemical cycle [3]. Oxygen and carbon dioxide are the two most important

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gases and, in this study we focus our attention on the roles played by carbon dioxide in the open Mediterranean waters in front of Egypt.

Carbon dioxide is transferred into the seawater biosphere via both the photosynthesis of marine plants and the formation of carbonate shells by plants and animals, and therefore involved in the formation of both soft organic tissues and hard skeletal materials. As carbon dioxide is removed from seawater by the biological reactions, it is being continuously added from the atmosphere. At greater depths in the water column it is regenerated by the oxidative destruction of organic matter and so increases in concentration below the surface. SCOR (1995) [4] stated that typical water column profiles of carbon dioxide show depletion in the surface layers and an over all increase towards the base of the euphotic zone.

The Egyptian Mediterranean coast lies between longitudes 25° 30′ E and 34° E and extends north-word to latitude 33° N. Its water volume is about 225 km^3 and it has a surface area of about 155 km^2. The most striking features of this area are the presence of different water masses of mixed coverage. According to Said and Eid [5], these water masses are: 1) the surface water mass (SW; temperature 22–28 °C and maximum salinity 38.80–39.25 PSU), 2) the subsurface layer (SSW; 50–100 m deep, temperature 17–22 °C and minimum salinity 38.6–38.8 PSU), 3) the Levantine intermediate water mass (LIW; 150–400 m deep, temperature 15–17 °C and maximum salinity 38.9–39.1 PSU), 4) a mid-deep layer (MDW; 400–800 m deep, temperature 13.6–14.5 °C and salinity 38.75–38.87 PSU), and 5) a deep water mass (DW; 1000 m deep, temperature 13.3–13.5 °C and salinity 38.68–38.75 PSU). Four stations were chosen to represent this region to measure carbon dioxide content.

The present work represents the first investigation for measuring and evaluating the carbon dioxide components in the open Mediterranean Sea waters in front of Egypt. It also includes measuring and calculation of pH, total alkalinity, specific alkalinity, bicarbonate concentrations, total carbon dioxide, partial pressure of carbon dioxide and dissolved carbon dioxide at four locations to depths greater than 2000 m.

2. Material and methods

Samples were collected in the period October–November 2001 on board the R/V Meteor M51/2. Four deep stations located between latitudes 32° 31′ 22 and 33° 14′ 91 N and longitudes 25° 31′ 10 and 29° 59′ 84 E were selected to represent CO_2 components in the SE Mediterranean open waters in front of the Egyptian coastal water (figure 1). These stations are, St. 546 north of Rosetta branch of the River Nile (at 2700 m deep), Dabaa St. 547 sampled until depth 3100 m and Salloom Sts. 549 and 550 sampled at depth 2670 and 2330 m, respectively. Seawater samples were collected with a general oceanic Rosette equipped with 24 Niskens bottles of 5-litre volume each. Seawater was sampled at 10–11 depths at each station to represent the surface, subsurface, middle and deep waters of the region. Samples for the determination of pH, total alkalinity and carbon dioxide were taken first using a 250-ml acid washed polyethylene bottle pre-washed several times for each sample. The pH was measured, using a glass electrode and electrometer type pH meter Orion Research Model 201 with a precession of ±0.01 unit. Total alkalinity was determined in a portion of a 100-ml water sample after mixing with 25 or 30 ml of 0.01N HCl. The pH of the resulting solution was measured. The standard acid in excess of that required to titrate the sample to the CO_2 inflection point was computed from the knowledge of this pH and an empirical factor. This excess acid was then subtracted from 2.5 or 3 meq l^{-1} depending on the amount of 0.01N HCl initially added and the total alkalinity

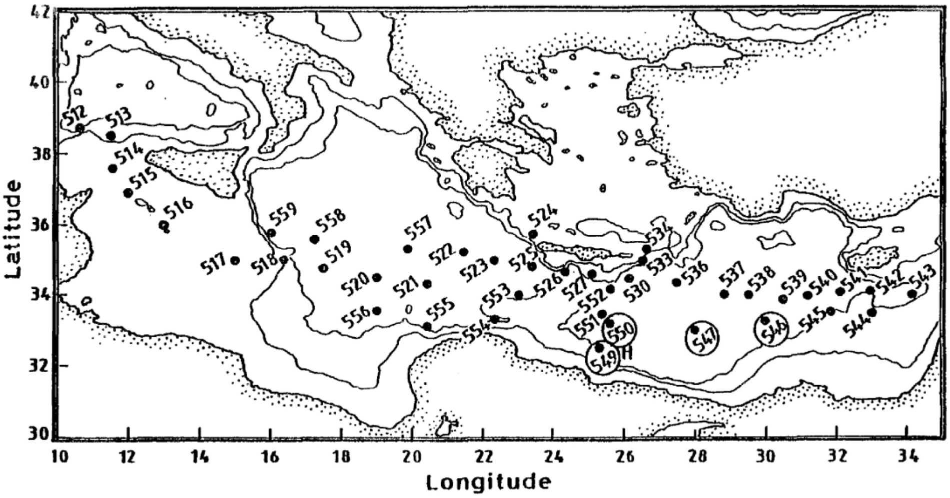

Figure 1. Sampling stations for cruise M51/2 in the Eastern Mediterranean, including 4 stations in front of Egypt.

was thus evaluated [6]:

$$\text{Total alkalinity} = 2.5 - (1250\ (\text{H}+/\text{F}) \quad \text{for 25 ml 0.01N HCl}$$

$$= 3.0 - (1300\ (\text{H}+/\text{F}) \quad \text{for 30 ml 0.01N HCl},$$

where: (H+ $= 10^{-\text{pH}}$ and F = factor affected by temperature and salinity.)

Total carbon dioxide (T_{CO_2}), partial pressure (P_{CO_2}), dissolved CO_2 (D_{CO_2}) and bicarbonate ions were obtained using the tables calculated by Strickland and Parsons [6].

The surface water mass (0–50 m) and the subsurface water mass data (50–100 m) were added together to form one water mass which occupies the layer from surface to about 100 m deep and named surface water mass (SW).

The *t*-test and ANOVA analysis at the 95% confidence level were used in statistical comparison for the chemical characterization of the water body.

3. Results and discussion

Table 1 illustrates the average values of the measured parameters at different water masses in the studied stations.

3.1 *Surface water mass (SW)*

SW mass (0–50 m) and the subsurface water mass (50–100 m) were added together to form one water mass which occupies the layer from the surface to about 100 m deep. The levels of surface water temperature ranged from 12.34 ± 1.5 to 23.9 ± 0.0 °C, while salinity values ranged from 38.98 ± 0.2 to 39.20 ± 0.0 PSU.

There are no significant differences between the values of all measured parameters at each station. The average concentrations of these parameters were pH (8.24 ± 0.06), total alkalinity (1.92 ± 0.53 meq l^{-1}), specific alkalinity (0.09 ± 0.03), bicarbonate (1.80 ± 0.51 mM l^{-1}), total CO_2 (1.60 ± 0.45 mM l^{-1}), P_{CO_2} ($0.24 \pm 0.09 \times 10^{-3}$ atmosphere) and D_{CO_2} (7.68 ± 2.98 mM l^{-1}). The net flux of CO_2 into or out of the sea across the air–sea interface is driven

Table 1. The average values of pH, total alkalinity (TA., meq l^{-1}), specific alkalinity (Sp.A., ratio), bicarbonate (mM l^{-1}), total CO_2 (T_{CO_2}, mM l^{-1}), partial pressure (P_{CO_2}, atmosphere), dissolved CO_2 (D_{CO_2}, mM l^{-1}) at different water masses in the studied stations in November 2001.

Water masses	pH	TA.	Sp.A.	Bicarbonate	T_{CO_2}	$P_{CO_2} \times 10^{-3}$	D_{CO_2}
Station 546 – North of Rosetta Branch							
Surface water mass	8.22 ± 0.11	1.06 ± 0.55	0.05 ± 0.03	0.95 ± 0.54	0.85 ± 0.47	0.11 ± 0.05	3.63 ± 1.53
Levantine intermediate water mass	8.28 ± 0.03	0.74 ± 0.0	0.04 ± 0.0	0.06 ± 0.0005	$0.58 \pm 5 \times 10^{-3}$	0.07 ± 0.01	2.64 ± 0.38
Mid-deep water mass	8.21 ± 0.0	1.16 ± 0.13	0.06 ± 0.0006	1.06 ± 0.13	0.98 ± 0.12	0.14 ± 0.02	5.47 ± 0.59
Deep water mass	8.16 ± 0.06	0.48 ± 0.06	0.02 ± 0.0003	0.39 ± 0.68	0.36 ± 0.07	0.06 ± 0.02	2.30 ± 0.72
Station 547 – North of Dabaa							
Surface water mass	8.24 ± 0.04	2.22 ± 0.12	0.11 ± 0.001	2.09 ± 0.12	1.84 ± 0.12	0.23 ± 0.01	7.51 ± 0.66
Levantine intermediate water mass	8.35 ± 0.13	2.45 ± 0.15	0.12 ± 0.001	2.31 ± 0.18	2.04 ± 0.23	0.24 ± 0.11	8.58 ± 3.98
Mid-deep water mass	7.88 ± 0.32	1.64 ± 0.51	0.08 ± 0.02	1.58 ± 0.55	1.54 ± 0.59	0.69 ± 0.56	27.47 ± 22.07
Deep water mass	8.15 ± 0.17	0.87 ± 0.24	0.04 ± 0.01	0.78 ± 0.23	0.73 ± 0.21	0.12 ± 0.07	4.97 ± 2.72
Station 549 – In front of Salloom							
Surface water mass	8.30 ± 0.00	2.44 ± 0.08	0.12 ± 0.0004	2.3 ± 0.08	2.03 ± 0.07	0.23 ± 0.0008	7.51 ± 0.45
Levantine intermediate water mass	8.27 ± 0.01	1.89 ± 0.6	0.09 ± 0.03	1.76 ± 0.56	1.57 ± 0.5	0.18 ± 0.06	6.32 ± 1.98
Mid-deep water mass	8.24 ± 0.03	2.38 ± 0.01	0.11 ± 0.0	2.28 ± 0.0005	$2.09 \pm 5 \times 10^{-3}$	0.26 ± 0.03	10.4 ± 1.25
Deep water mass	8.22 ± 0.01	2.45 ± 0.20	0.12 ± 0.0009	2.35 ± 0.20	2.16 ± 0.18	0.31 ± 0.03	12.32 ± 1.02
Station 550 – In front of Salloom							
Surface water mass	8.15 ± 0.26	1.96 ± 0.42	0.093 ± 0.02	1.85 ± 0.43	1.70 ± 0.4	0.37 ± 0.28	12.06 ± 8.66
Levantine intermediate water mass	8.28 ± 0.02	2.32 ± 0.07	0.11 ± 0.0003	2.19 ± 0.07	1.95 ± 0.06	$0.22 \pm 6 \times 10^{-3}$	7.88 ± 0.27
Mid-deep water mass	8.29 ± 0.01	2.79 ± 0.17	0.13 ± 0.0007	2.67 ± 0.2	2.4 ± 0.15	0.27 ± 0.01	10.83 ± 0.39
Deep water mass	$8.26 \pm 4 \times 10^{-3}$	2.29 ± 0.16	0.11 ± 0.0006	2.17 ± 0.16	1.95 ± 0.13	0.22 ± 0.02	8.73 ± 0.61

by the difference between the partial pressure of CO_2 in the atmosphere and the equilibrium partial pressure of CO_2 in the surface water [7].

Two factors affect partial pressure of CO_2 in surface water: temperature (CO_2 becomes less soluble in warmer waters and more soluble in cold waters) and biological effects (CO_2 is used by phytoplankton during photosynthetic process).

3.2 *Levantine intermediate water (LIW)*

LIW (150–400 m) was characterized by a salinity of 38.9–39.1 PSU and a temperature of 15–17 °C.

Station 547 in front of Dabaa was characterized by the highest values of pH (8.35 ± 0.13), total alkalinity ($2.45 \pm 0.15\,\mathrm{meq\,l^{-1}}$), bicarbonate ($2.31 \pm 0.18\,\mathrm{mM\,l^{-1}}$) and total CO_2 ($2.04 \pm 0.23\,\mathrm{mM\,l^{-1}}$). The same patterns were also encountered in front of Salloom (at station 550), with an increase in total alkalinity ($2.32 \pm 0.07\,\mathrm{meq\,l^{-1}}$), total CO_2 ($1.95 \pm 0.06\,\mathrm{mM\,l^{-1}}$) and P_{CO_2} ($0.22 \pm 6 \times 10^{-3}$ pressure). These high values, compared to those encountered in the surface zone or other sites, may be due to the fact that this water mass is characterized by a sharp decrease in the fluorimetric measurements, reflecting the decrease of phytoplankton biomass [8].

The average values of the investigated parameters in the LIW were, pH (8.30 ± 0.03), total alkalinity ($1.85 \pm 0.67\,\mathrm{meq\ l^{-1}}$), specific alkalinity (0.09 ± 0.03), bicarbonate ($1.58 \pm 0.9\,\mathrm{mM\,l^{-1}}$), total CO_2 ($1.53 \pm 0.58\,\mathrm{mM\,l^{-1}}$), P_{CO_2} ($0.18 \times 10^{-3} \pm 0.06$) and dissolved CO_2 ($6.35 \pm 2.30\,\mathrm{mM\,l^{-1}}$).

The vertical distribution of alkalinity in this water mass indicates that there was a gradual increase in alkalinity with depth below the SW. The distribution pattern of the measured variables in the LIW is controlled by an interaction or balance between the circulation and biological activity. It is reported [9] that the Atlantic water mass enters the eastern Mediterranean through the Strait of Sicily and its salinity and depth increase as it flows eastward. In summer, because of the increased evaporation of Atlantic water, it is capped with a layer of more saline and warmer water, the LSW. In winter, the AW mass is essentially LSW. The Levantine intermediate water is formed in the Levantine Basin and flows into the western Mediterranean and from there to Atlantic Ocean [9].

3.3 *Mid-deep water (MDW)*

This water mass is found at 400–800 m deep and was characterised by an average temperature of 13.6–14.5 °C and salinity of 38.75–38.87 PSU.

At station 547, north of Dabaa and in front of Mersa Matrouh, pH encountered the lowest value (7.88 ± 0.32) whereas an increase in the P_{CO_2} and dissolved CO_2 ($0.69 \pm 0.56 \times 10^{-3}$ atmosphere and $27.47 \pm 22.07\,\mathrm{mM\,l^{-1}}$, respectively) was reported. This pattern could be as a result of the indirect effect of pH on the dissolution of CO_2, since pH is considered as one of the most important factors affecting CO_2 dissolution in marine environment. The indirect relation between pH and total CO_2 of the marine environment is the result of shell formation and the synthesis of particulate organic matter [10].

The average values of total alkalinity ($1.99 \pm 0.63\,\mathrm{meq\,l^{-1}}$), specific alkalinity (0.095 ± 0.03), total CO_2 ($1.75 \pm 0.54\,\mathrm{mM\,l^{-1}}$), P_{CO_2} ($0.34 \pm 0.21 \times 10^{-3}$ pressure) and dissolved CO_2 ($13.55 \pm 8.31\,\mathrm{mM\,l^{-1}}$) were higher than values reported in the other water masses. These maxima values could be determined by the biological activities. It transports fixed carbon from LIW via the vertical gravitational settling of the biogenic debris produced in the SW and LMW. Most of particulate organic matter was destroyed in this water mass and recycled there [8]. The greatest effect of the biological activities is to reduce the P_{CO_2} in SW causing an enhancement in the drawdown of CO_2 from the atmosphere, initiated by phytoplankton growth. Riebesell *et al.* [11], Hesshaimer *et al.* [12], and Fahmy [8] found that at this water mass the nutrient concentrations increased rapidly with depth following the remineralization of sinking detritus and the decomposition of organic matter reached to the MDW. The low value of pH (8.14 ± 0.15) recorded at this water mass may be attributed to the increase in the dissolution rate of carbon dioxide causing an increase in total alkalinity content or vice versa.

3.4 *Deep water (DW)*

This water mass of the SE Mediterranean derived to a large extent from the Aegean Sea, which replaced or masked the Adriatic deep waters [13, 14]. Steinfeldt [15], estimating the age and age spectra of the EMDW, suggested that the most probable age can be estimated as the transit time of the deep water from its source in the Adriatic Sea to the specific region. These time-scales are 1.5, 4.5 and about 20 years for the northern and central Ionian and the Levantine, respectively. The mean spreading velocity of EMDW is approximately 0.4 cm/s based upon a distance between the Adriatic and the Levantine (about 2500 m).

DW is located at more than 1000 m deep and is characterised by a temperature ranging from 13.3 to 13.5 °C and salinity from 38.68 to 38.75 PSU.

At station 546, north of Rosetta Branch, all parameters showed the lowest values of: pH (8.16 ± 0.06), total alkalinity ($0.48 \pm 0.06\,\mathrm{meq\,l^{-1}}$), specific alkalinity ($0.02 \pm 2.9 \times 10^{-3}$), bicarbonate ($0.39 \pm 0.68\,\mathrm{mM\,l^{-1}}$), total CO_2 ($0.36 \pm 0.07\,\mathrm{mM\,l^{-1}}$), P_{CO_2} ($0.06 \pm 0.02 \times 10^{-3}$) and dissolved CO_2 ($2.30 \pm 0.72\,\mathrm{mM\,l^{-1}}$). Also, the average values resulted the lowest of all the other water masses (average values, pH: 8.20 ± 0.04, total alkalinity: $1.52 \pm 0.86\,\mathrm{meq\,l^{-1}}$, specific alkalinity: 0.07 ± 0.04, bicarbonate: $1.42 \pm 0.85\,\mathrm{mM\,l^{-1}}$, total CO_2: $1.30 \pm 0.77\,\mathrm{mM\,l^{-1}}$, P_{CO_2}: $0.18 \pm 0.09 \times 10^{-3}$ and dissolved CO_2: $7.08 \pm 3.79\,\mathrm{mM\,l^{-1}}$). These low values may be due to the fact that within the deep-water reservoir, CO_2 can be utilized in the dissolution of sedimentary carbonates, with the result that when the deep water returns to the surface it can absorb more CO_2 from the atmosphere [16, 17]. The precipitation of calcium carbonate decreases total alkalinity and as a result it is a measure of calcification and other biogeochemical processes involving species of CO_2. Campbell [7] pointed out that processes such as the precipitation and dissolution of calcium carbonate and the removal and regeneration of nitrate affect alkalinity and contribute to its non-conservative behaviour. It is also found that in deep waters the increase in alkalinity reflects the presence of excess calcium which is released as a result of the increasing extent of carbonate dissolution with depth in the water column and in the underlying sediment [18].

The vertical distribution of CO_2 components at each station of the Mediterranean Sea deep waters in front of Egypt is shown in figure 2. It is observed that at station 547 which is located north of Dabaa, total CO_2 and P_{CO_2} values increased with depth up to 1000 m depth. This is attributed to seawater circulation pattern at this station and water mass movement. This is also influenced most strongly by the operation of the biological pump. Sarmiento *et al.* [19] found that less than 5–10% of surface production which escapes recycling is transported to deep water, but most of the organic debris transported down the water column by the biological pump is destroyed in the upper water layer, less than 1000 m, leading to the release of CO_2 components into the water. Below this maximum the values of P_{CO_2} and total CO_2 fall and then either fall further towards deeper water, more than 1000 m, or become more or less constant with depth. Skirrow [20] found that in deep water which is out of contact with the atmosphere, total CO_2 is changed by the mixing of different water masses, by the dissolution of carbonate shells, and by the decomposition of the relatively small amount of organic matter that reaches these depths.

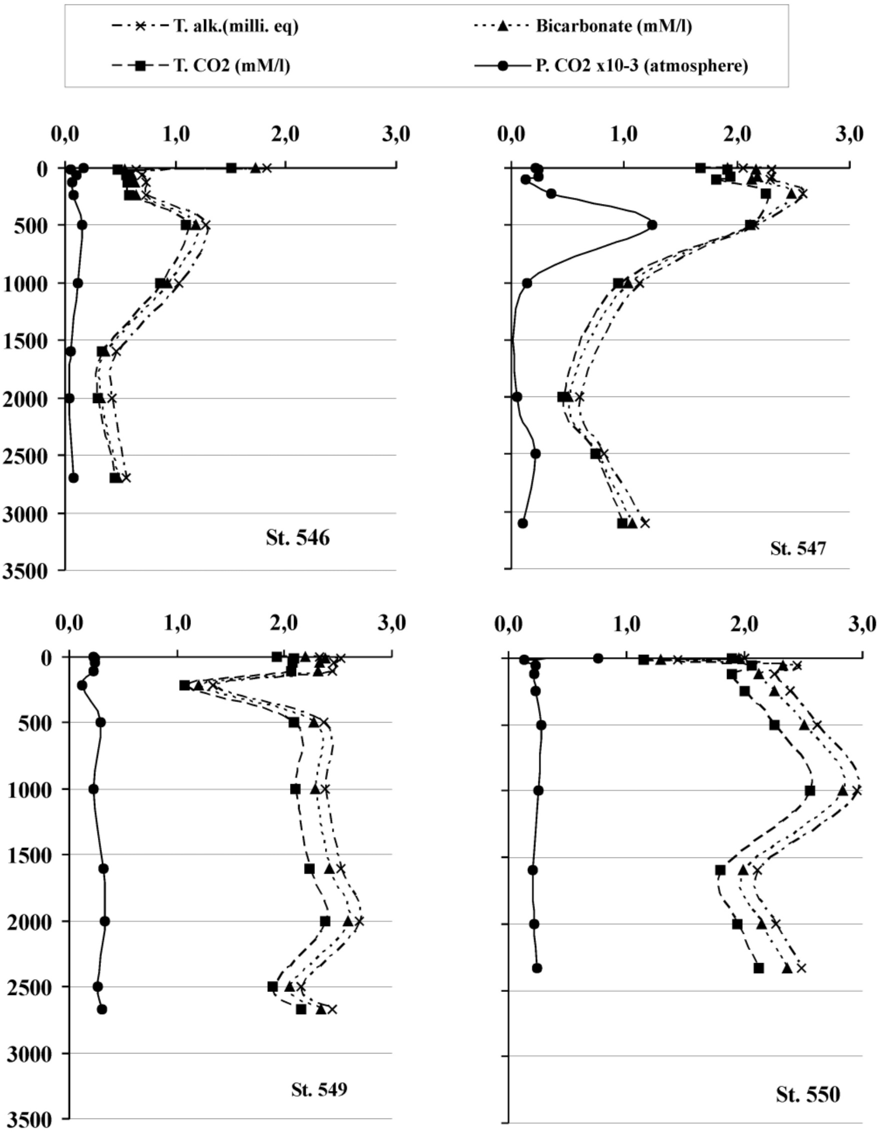

Figure 2. The vertical distribution of CO_2 components at each station of the Mediterranean Sea deep waters in front of Egypt (M51/2 Nov. 2001).

The correlation matrices between parameters in the investigated area were calculated. There are well-established positive relations between total alkalinity and total CO_2 ($r = 1.0$), P_{CO_2} ($r = 0.44$), dissolved CO_2 ($r = 0.43$) and bicarbonate ($r = 1.0$). This means that total alkalinity is the main factor affecting carbon dioxide content in the water and vice versa. A stepwise regression analysis technique was applied by using TA as dependent and other studied parameters as independent variable (equation 1):

$$\begin{aligned} \mathrm{TA} = {} & -0.508 + 0.00238\,\mathrm{Temp} - 0.0227\,\mathrm{DO} - 0.00090\,\mathrm{S} + 0.0872\,\mathrm{pH} + 1.35\,\mathrm{HCO_3} \\ & - 0.383\,\mathrm{T_{CO_2}} + 0.0341\,\mathrm{P_{CO_2}} \times 10^{-3} + 0.00040\,\mathrm{D_{CO_2}}. \end{aligned} \tag{1}$$

A negative correlation is found between pH and P_{CO_2} ($r = -0.75$), dissolved CO_2 ($r = -0.75$). This is due to the fact that pH is a key to understanding the change in the CO_2 equilibrium between the atmosphere and seawater CO_2. The amount of CO_2 in seawater generally exceeds photosynthetic demand, so the changes in pH that occur due to photosynthetic removal of CO_2 are relatively small [21, 22]. The regression equation (2), using pH as dependent and other studied parameters as independent is:

$$\begin{aligned} \text{pH} = {} & 7.83 - 0.000006\ \text{Depth} + 0.0065\ \text{Temp.} - 0.056\ \text{DO} + 0.0040\ \text{S} + 3.95\ \text{TA} \\ & - 4.72\ H_{CO_3} + 0.908\ T_{CO_2} - 0.674\ P_{CO_2} \times 10^{-3} + 0.0035\ D_{CO_2}. \end{aligned} \tag{2}$$

It is found that there is a negative correlation between depth, temperature ($r = -0.71$), salinity ($r = -0.4$) and dissolved oxygen ($r = -0.65$). This means that with increasing depth temperature, salinity and dissolved oxygen content decrease.

Bicarbonate concentrations in the studied area are positively correlated with total CO_2 ($r = 0.99$), P_{CO_2} ($r = 0.46$) and dissolved CO_2 ($r = 0.45$). These correlations suggest that carbon dioxide species are affected greatly by bicarbonate content. Equation 3 illustrates the regression equation between bicarbonate and different measured parameters:

$$\begin{aligned} HCO_3 = {} & 0.310 - 0.000000\ \text{Depth} - 0.00112\ \text{Temp.} + 0.0125\ \text{DO} + 0.00070\ \text{S} - 0.0550\ \text{pH} \\ & + 0.711\ \text{TA} + 0.320\ T_{CO_2} - 0.0329\ P_{CO_2} \times 10^{-3} - 0.00021\ D_{CO_2}. \end{aligned} \tag{3}$$

A stepwise regression analysis technique was applied by using the other measured parameters (temperature, dissolved oxygen, salinity, total CO_2, P_{CO_2} and D_{CO_2}) as dependent and other studied parameters as independent variable (equations 4–8). These equations were calculated by Minitab version 13 program.

$$\begin{aligned} \text{Temp.} = {} & -17.1 - 0.00039\ \text{Depth} + 8.71\ \text{DO} - 0.250\ \text{S} + 0.084\ \text{pH} + 1.40\ \text{TA} \\ & - 1.25\ HCO_3 - 0.19\ T_{CO_2} + 0.80\ P_{CO_2} \times 10^{-3} - 0.0173\ D_{CO_2} \end{aligned} \tag{4}$$

$$\begin{aligned} \text{DO} = {} & 1.85 + 0.000044\ \text{Depth} + 0.114\ \text{Temp.} + 0.0320\ \text{S} - 0.0095\ \text{pH} \\ & - 0.175\ \text{TA} + 0.183\ HCO_3 - 0.006\ T_{CO_2} - 0.045\ P_{CO_2} \times 10^{-3} \\ & + 0.00088\ D_{CO_2} \end{aligned} \tag{5}$$

$$\begin{aligned} \text{S} = {} & 27.1 - 0.000132\ \text{Depth} - 0.360\ \text{Temp.} + 3.52\ \text{DO} + 0.074\ \text{pH} \\ & - 0.77\ \text{TA} + 1.13\ HCO_3 - 0.40\ T_{CO_2} + 0.08\ P_{CO_2} \times 10^{-3} \\ & + 0.0011\ D_{CO_2} \end{aligned} \tag{6}$$

$$\begin{aligned} T_{CO_2} = {} & -0.394 + 0.000001\ \text{Depth} - 0.0013\ \text{Temp.} - 0.003\ \text{DO} - 0.0019\ \text{S} \\ & + 0.0803\ \text{pH} - 1.53\ \text{TA} + 2.43\ HCO_3 + 0.135\ P_{CO_2} \times 10^{-3} \\ & - 0.00007\ D_{CO_2} \end{aligned} \tag{7}$$

$$\begin{aligned} P_{CO_2} \times 10^{-3} = {} & 0.894 - 0.000002\ \text{Depth} + 0.0099\ \text{Temp.} - 0.043\ \text{DO} + 0.0007\ \text{S} \\ & - 0.110\ \text{pH} + 0.251\ \text{TA} - 0.459\ HCO_3 + 0.248\ T_{CO_2} \\ & + 0.0232\ D_{CO_2} \end{aligned} \tag{8}$$

$$\begin{aligned} \text{D. } CO_2 = {} & -9.9 - 0.000011\ \text{Depth} - 0.364\ \text{Temp.} + 1.42\ \text{DO} + 0.016\ \text{S} + 0.96\ \text{pH} \\ & + 4.9\ \text{TA} - 5.0\ HCO_3 - 0.2\ T_{CO_2} + 39.2\ P_{CO_2} \times 10^{-3}. \end{aligned} \tag{9}$$

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