Mediterranean Marine Science

Vol 7, No 1 (2006)

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doi: 10.12681/mms.178

Mediterranean Marine Science
Volume 7/1, 2006, 63-78

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Abstract

Data on the distribution of dissolved inorganic carbon (measured as TCO_2) and related parameters in the Thermaikos Gulf were obtained during May 1997. High TCO_2 concentrations were recorded close to the bottom, especially in the northern part of the gulf, as a result of organic matter remineralisation. The positive relatively good correlation between TCO_2 and both apparent oxygen utilisation (AOU) and phosphate at the last sampling depth confirmed the regenerative origin of a large proportion of TCO_2. The comparatively conservative behaviour of alkalinity, together with the relatively low value of the homogenous buffer factor β ($\beta = \partial lnfCO_2/\partial lnTCO_2$) revealed that calcification or carbonate dissolution takes place on a very small scale, simultaneously with the organic carbon production. The correlations between fCO_2 and chlorophyll α, as well as AOU and the surface temperature, revealed that the carbon dioxide fixation through the biological activity is the principal factor that modulates the variability of fCO_2.

A rough first estimate of the magnitude of the air-sea CO_2 exchange and the potential role of the Thermaikos Gulf in the transfer of atmospheric CO_2 was also obtained. The results showed that during May 1997, the Thermaikos Gulf acted as a weak sink for atmospheric CO_2 at a rate of -0.60 - -1.43 mmol m^{-2} d^{-1}, depending on which formula for the gas transfer velocity was used, and in accordance to recent reports regarding other temperate continental shelves.

Extensive study of the dissolved inorganic carbon and related parameters, and continuous ship-board measurements of fCO_2^a and fCO_2^w during all seasons are necessary to safely quantify the role of the Thermaikos Gulf in the context of the coastal margins CO_2 dynamics.

Keywords: Eastern Mediterranean; Thermaikos Gulf; Continental shelf; Dissolved inorganic carbon; Air-sea CO_2 exchange.

Introduction

Continental shelves and slopes have frequently been considered as a small area of the ocean and therefore, unimportant in terms of the global carbon cycle. Although ocean margins comprise less than 10% of the surface area of the world's oceans, they account for up to one-third of global marine primary production (ALONGI 1998), ~80%

of organic matter burial, ~90% of sedimentary mineralisation and ca 50% of calcium carbonate deposition (PERNETTA & MILLIMAN, 1995). They also exchange nutrients and inorganic and organic carbon with the open ocean intensively across marginal boundaries, thus constituting the major link between the terrestrial and the open ocean environments and consequently play a key role in the global carbon cycle by linking the terrestrial, oceanic and atmospheric reservoirs. However, nowadays there is a great uncertainty about the overall role of coastal ecosystems in global carbon cycling and the question of whether shelf seas act as a sink or source for carbon dioxide still remains open.

Coastal waters are characterised by large spatial and temporal variations of the parameters of the CO_2/carbonate system, associated with intensive physical, chemical and biological processes occurring in these sites. The role of the shelves in the inorganic carbon cycle is uncertain because it results from the integration of production/remineralization/export of organic carbon, burial/dissolution of carbonates in the shallow sediment and input of inorganic carbon from rivers and coastal upwelling. One major challenge in studying the carbon cycling of coastal areas arises from the complexity and heterogeneity of the systems. Field data on the distribution of carbonate system species are needed in order to provide information on the carbon cycling and the biogeochemical processes in the coastal zone, as well as to assess the effective role of the coastal zone in the global carbon cycle.

In contrast to the open ocean, the dynamics of the CO_2/carbonate system in coastal regions have only begun to receive more attention in recent years (BAKKER *et al.,* 1996; FRANKIGNOULLE *et al.,* 1996; TSUNOGAI *et al.,* 1999; FRANKIGNOULLE and BORGES, 2001; DEGRANDPRE *et al.,* 2002; IANSON *et al.,* 2003; WANG *et al.,* 2005; BOZEC *et al.,* 2005 and references therein). In the Mediterranean Sea a few measurements on the carbonate system mainly focused on its western part, have been published (MILLERO *et al.,* 1979; COPIN-MONTEGUT, 1993; DELGADO & ESTRADA, 1994; COPIN-MONTEGUT & BEGOVIC, 2002 and references therein), as well as some on the northern Adriatic (SOUVERMEZOGLOU & KRASAKOPOULOU, 1999).

In this work we attempt to study, for the first time, the distribution of the inorganic carbon species and their relationships with other properties such as salinity, temperature, dissolved oxygen and chlorophyll *a* in an eastern Mediterranean regime. In addition, the air-sea CO_2 flux is estimated using an indirect method, in order to assess the potential role of the Thermaikos Gulf as a source or sink of atmospheric CO_2 during late spring of 1997.

Study area

The Thermaikos Gulf is an elongated basin characterised by an extensive shelf (depths <200m) located in the NW Aegean Sea. The northern part of the gulf (inner Thermaikos Gulf) comprises the Bay of Thessaloniki, where the city of Thessaloniki (population ca 1.2 million) is found, and the Gulf of Thessaloniki (Fig.1). Three major rivers Axios, Aliakmon, Pinios, and two smaller ones, Loudias and Gallikos, discharge along its northern and western boundaries and transport significant nutrient loads, which eventually enter the coastal ecosystem, mostly through episodic flooding events (KARAGEORGIS *et al.,* 2005). In addition to the riverine nutrients inputs, the gulf receives the urban effluents from the city of Thessaloniki and the adjacent industrial zone. Due to the increased influx of inorganic and organic material at the shelf area, the inner part of the gulf exhibits higher plankton biomass and productivity than the oligotrophic Aegean Sea and the trophic status of the area is characterised as a eutrophic one (GOTSIS-SKRETAS & FRILIGOS, 1990; BALOPOULOS & FRILIGOS 1993; PAGOU *et al.,* 2000; PAGOU, 2005).

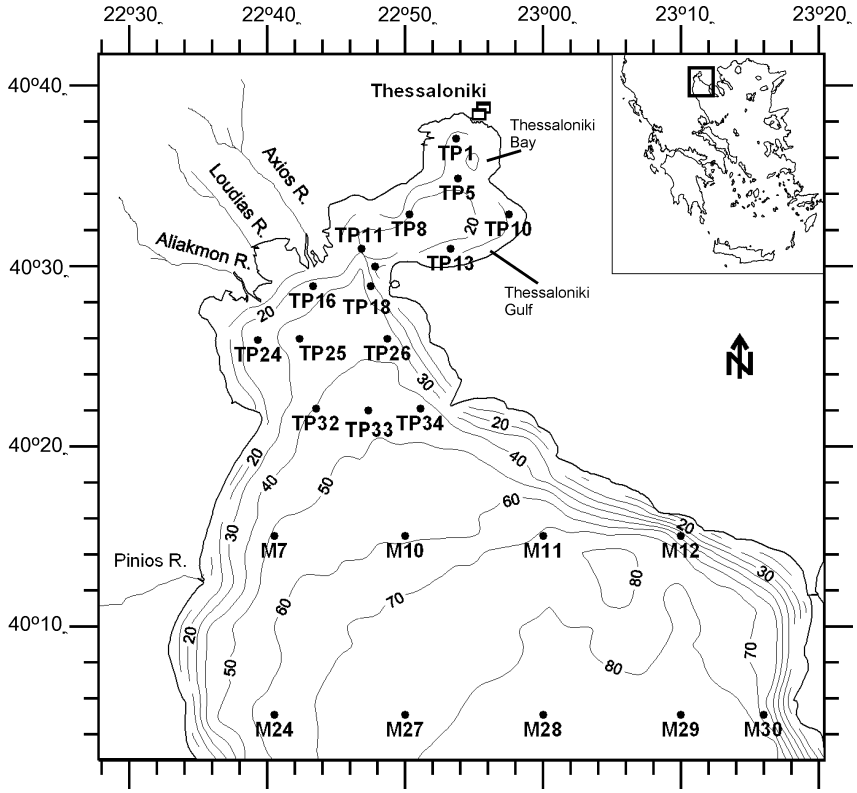

Fig. 1: Locations of TCO_2 sampling stations during the May 1997 cruise and bathymetry (depth contours in m) of the study area (KARAGEORGIS *et al.,* 2003).

Considerable production of carbon dioxide, particularly in the bottom layer, is to be expected from the decomposition of the external imported organic matter (mainly from the rivers and the sewage pipes) and of that produced *in situ* in the Thermaikos Gulf.

The forcing mechanisms that control shelf circulation in the Gulf of Thermaikos are air-sea interaction (wind and surface heating/cooling), land-sea interaction (buoyancy due to river discharge), and coastal deep-sea interaction (intrusion of Aegean waters onto the continental shelf). Topography also plays an important role due to the presence of both gradual and steep shelf slopes (KONTOYIANNIS *et al.,* 2003). Generally, saline waters from the Aegean enter the gulf from its central and eastern part, flow northwards and as they turn towards the southwest, they mix with freshwater originating from the rivers and flow southwards along the western coastline (ROBLES *et al.,* 1983; POULOS *et al.,* 2000; HYDER *et al.,* 2002).

Materials and Methods

Sampling

Sampling was conducted during May 1997 with *R/V Aegaeo* within the framework of the EU Metro-Med project (Dynamics of matter transfer and biogeochemical cycles: Their modelling in coastal systems of the Mediterranean Sea). Twenty-four stations were sampled in the Thermaikos Gulf, covering the areas of the Thessaloniki Bay and the Thessaloniki Gulf (TP stations) and the continental shelf (M stations) (Fig. 1). Seawater samples were collected with a General

Oceanics rosette equipped with 12 Niskin bottles of 10 L mounted on a SeaBird SBE-911+ conductivity-temperature-depth (CTD) profiler. Two depths (surface and bottom) were sampled in most stations and three to four depths in the stations TP5, TP25, M24; a total of 52 samples were analysed. The seawater samples were drawn into 500-1000 mL borosilicate glass bottles sealed with glass stoppers according to the collection methods of DOE (1994). The samples were poisoned with 1mL/L of saturated $HgCl_2$ to prevent further biological activity, stored at room temperature away from light and analysed on shore the as soon as possible. The apparent oxygen utilisation (AOU) was calculated according to the difference of the measured oxygen values to the oxygen saturation given by the algorithm of MILLERO (1986).

Determination of TCO_2 and TA

The carbon dioxide system in the oceans can be characterized using any two of the four measurable parameters, pH, total alkalinity (TA), partial pressure (pCO_2) or fugacity (fCO_2) of carbon dioxide and the total inorganic carbon (TCO_2), providing that constants are available for the other acid/base species in seawater. Dissolved CO_2 constitutes less than 1% of the dissolved inorganic carbon content of seawater, which otherwise consists of bicarbonate, carbonate and a negligible amount of carbonic acid: $TCO_2 = [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$. Dissociation constants of carbonic acid are needed to calculate the components of the CO_2 system from these measurements.

Dissolved Inorganic Carbon (TCO_2) and Total Alkalinity (TA) were measured simultaneously with a precise potentiometric method, based on the analytical and calculation procedure described by DYRSSEN & SILLEN (1967), EDMOND (1970) and BRADSHAW *et al.* (1980 & 1981). The seawater is considered as a weak base and is titrated by hydrochloric acid 0.1 N. The progress of titration is monitored using a glass electrode/reference electrode pH cell. The TA corresponds to the carbonic acid endpoint and the TCO_2 concentration is computed by the difference between the two endpoints. The two endpoints of the titration are calculated using a modified Gran approach, a procedure recognised by DOE (1994). The analytical precision on replicate seawater samples was about 0.3%. The results are expressed in µmol/kg for the TCO_2 and µeq/kg for the TA. The system was calibrated using certified reference material (CRM) supplied by Dr A.G. Dickson of Scripps Institution of Oceanography, La Jolla, CA. The fugacity of carbon dioxide (fCO_2) was calculated from TA and TCO_2 measurements and the dissociation constants of carbonic acid of MEHRBACH *et al.*, (1973) and the solubility constants of WEISS & PRICE (1980) using the software of LEWIS & WALLACE (1998). The fCO_2 at 1 atm total pressure is 0.3-0.4% lower than its partial pressure (pCO_2) due to the non-ideal behaviour of carbon dioxide.

Results and Discussion

Spatial trends in TCO_2 concentrations

Dissolved inorganic carbon concentrations in the Thermaikos Gulf ranged from 2351 µmol/kg at the surface of TP11 to 2706 µmol/kg close to the bottom of TP5 (Thessaloniki Bay); the bottom samples of the same station also showed the lowest values of dissolved oxygen and the highest of nutrients (O_2<3.0ml/l, NO_3~0.04 µmol/L, SiO_4~5.9 µmol/L and PO_4~0.15 µmol/L). The surface values of TCO_2 are lower than those of the last depth (Fig. 2) reflecting the consumption of inorganic carbon by photosynthesis. In particular, the difference between the mean surface and the mean bottom values of TCO_2, 2451 and 2517 µmol/kg, respectively, is statistically significant at the 99% confidence level (n=24, *t*-test value=4.38). Lower surface TCO_2 concentrations appear near the north-western shore in response to the inflow of riverine waters. On the other hand, the increase of TCO_2 concentrations in the deeper layer, especially in the inner part of the gulf,

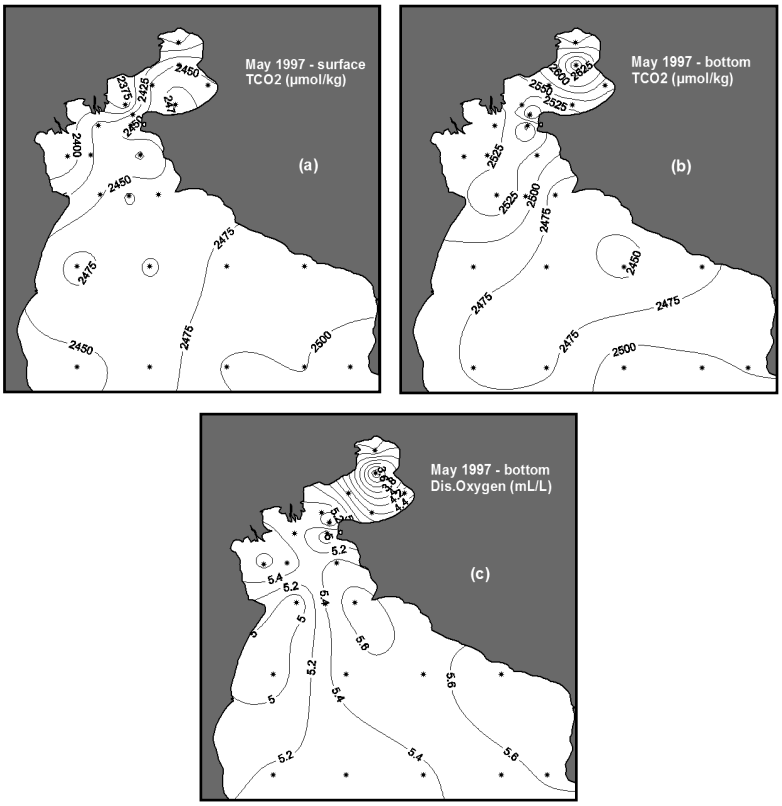

Fig. 2: Horizontal distribution of (a) TCO_2 at the surface layer, (b) TCO_2 at the last sampling depth and (c) dissolved oxygen at the last sampling depth in the Thermaikos Gulf during the May 1997 cruise.

implies that there is a formation of TCO_2 species in the near bottom waters. In addition, in the northern part of the gulf the bottom distribution of TCO_2 fits inversely with that of oxygen (Fig. 2), namely, the maximum TCO_2 values correspond to the minimum oxygen concentrations, implying a probable relationship between the two parameters.

Generally the concentrations of the TCO_2 found in the Thermaikos Gulf are significantly lower than those reported in the literature for the extreme environment of the Black Sea (GOYET *et al.,* 1991), in the same order of magnitude as those measured in the shallow northern Adriatic Sea (SOUVERMEZOGLOU & KRASAKOPOULOU, 1999) and higher than those reported for the central part of the NW Mediterranean Sea (COPIN-MONTEGUT & BEGOVIC, 2002).

Relationships of TCO_2 and TA with salinity and temperature

The variation of TCO_2 and TA with salinity has been described by different investigators using linear regressions (e.g. COPIN-MONTEGUT, 1993; BAKKER *et al.,* 1996; IANSON *et al.,* 2003; BOZEC *et al.,* 2005). If these relationships are truly linear then they suggest that both TCO_2 and TA concentrations are controlled by dilution (evaporation, precipitation, river runoff). Biological processes (uptake/release of TCO_2 during photosynthesis/respiration, $CaCO_3$ dissolution/formation) that occur at different water depths (and thus salinities) as well as surface TCO_2 exchange, which is temperature dependent, cause non linear variations of TCO_2 with

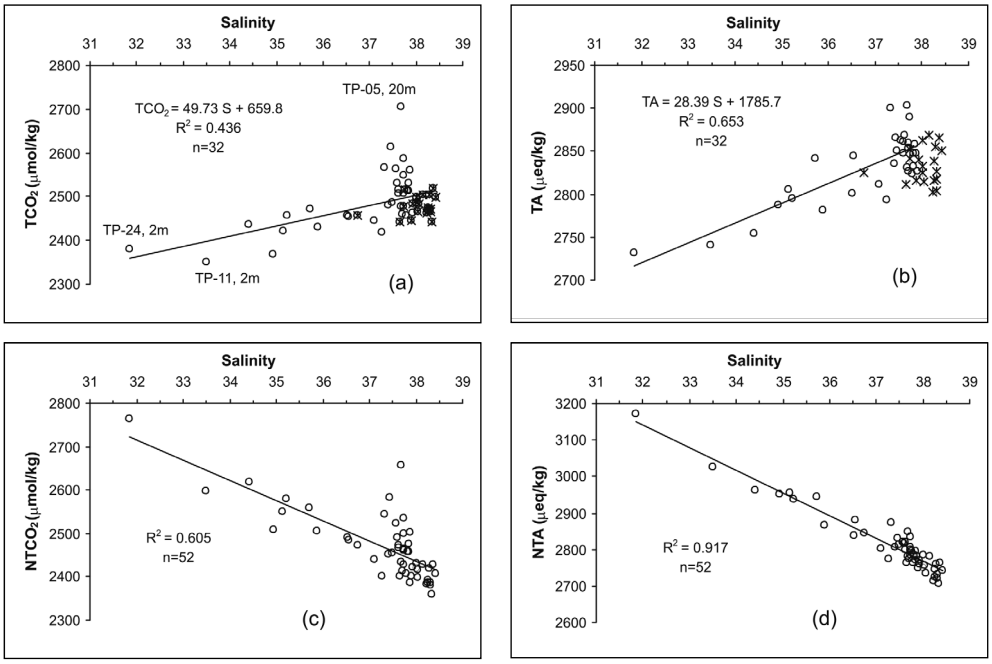

Fig. 3: Plots of (a) TCO_2 and (b) TA *vs*. salinity for all the samples of the TP- (circles) and M-stations (crosses). The regression lines and equations correspond to the TP-stations. (c) and (d) plots of normalized TCO_2 and TA *vs*. salinity.

salinity. In contrast to other variables of the CO_2/carbonate system (i.e. TCO_2, pH, fCO_2), biological processes such as photosynthesis and oxidation of organic matter have a rather small, negligible influence on the alkalinity (MILLERO *et al.,* 1998; BOEHME *et al.,* 1998). In the process of calcium carbonate dissolution/formation, TA would change with TCO_2 at a ratio of 2 to 1, due to the chemical equilibrium involved in solid carbonate production (i.e. $Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + CO_2 + H_2O$). In anoxic environments, TA change would be significant due to consumption of H^+ during anaerobic respiration. Since the waters of the inner Thermaikos Gulf are not anoxic, anaerobic respiration should be negligible.

Linear regressions (Model II) between our TCO_2 and TA data and salinity were calculated (Figs. 3a and b) in order to investigate the TCO_2 and TA characteristics of the water masses and to discuss deviations from linearity. In this figure we can distinguish the large difference between the TCO_2 and TA values per salinity of the TP-stations (circles) and those of the M-stations (crosses). Salinity ranged from 31.854 in front of the Aliakmon river estuary to 38.434 at 68m depth in the easternmost part of the study area (Station M30). Elevated values of both parameters appear at higher salinities; however, the data appear linear only when the TP-stations are considered. The lower values of the correlation coefficient which are obtained when the data of both the TP- and M-stations are used (0.273 for TCO_2 and 0.463 for TA) are probably due to the narrower variation of salinity of the M-stations. The M-stations are mainly influenced by the saline Aegean waters and exhibit higher salinity than the TP-stations, which are also influenced by the riverine water inputs. The weaker linear relationship between TCO_2 and salinity than is the case for TA is related to the larger modification of

TCO_2 by biological processes and to the air-sea exchange of CO_2. In addition, the stronger correlation of TA with salinity relative to TCO_2, indicates that calcium carbonate dissolution/precipitation processes are likely to be negligible and that dilution exerted the major control over TA in the Thermaikos Gulf during May 1997.

In order to remove the effects of changes in salinity due to mixing, fresh water runoff, precipitation and evaporation, the TCO_2 and TA values were normalized to a salinity of 37 representing the average salinity during the cruise; thus normalized data = measured data × 37/measured salinity. Consequently, changes in the normalized TCO_2 and TA can be attributed to the production and oxidation of plant material and formation and precipitation of $CaCO_3$. The salinity normalized data of both parameters ($NTCO_2$ and NTA) are inversely proportional to salinity (Figs. 3c and d). The strong linear relationship of NTA with salinity (r^2=0.917) confirms the almost conservative character of alkalinity that results from the mixing of the saline Aegean waters with the fresh waters of the inner gulf. The scatter around the line observed in the case of $NTCO_2$ gives evidence that additional processes occur and cause the variations of the TCO_2 concentrations in the study area during May 1997.

Relationships of TCO_2 with oxygen and nutrients

The enrichment of the bottom waters in TCO_2 is probably caused by the oxidation of the sinking organic matter. The organic material which is transported by the rivers and/or is produced *in situ*, falls into the deeper layer and undergoes remineralisation by consuming oxygen and producing equivalent amounts of carbon dioxide and of regenerated nutrients. According to the simplest stoichiometric formula of organic matter in the ocean [$(CH_2O)_{106}(NH_3)_{16}H_3PO_4$], an increase of 106 moles of carbon dioxide and a consumption of 138 moles of dissolved oxygen occurs, when this molecule is completely oxidised (AOU:C:N:P = -138:106:16:1; REDFIELD *et al.,* 1963). The positive linear correlation between TCO_2 and Apparent Oxygen Utilisation (AOU) for the samples collected at the last depth of the stations (Fig. 4a) confirms that carbon dioxide is released proportionately to the dissolved oxygen utilisation. The experimental ratio of carbon regeneration, i.e. the TCO_2 to AOU slope, is 1.63, almost double the predicted value from simple theory, 0.768 (stripped line, Fig.4a), but close to the value observed in the Jabuka Pit in the middle of the Adriatic Sea (KRASAKOPOULOU *et al.,* 2005). The TCO_2 data from the last sampling depth were also plotted against phosphate (Fig. 4b). Phosphate was chosen rather than nitrite+nitrate because these waters have the potential complication of denitrification in the water column (MARTY *et al.,* 2001), as well as in the sedi-

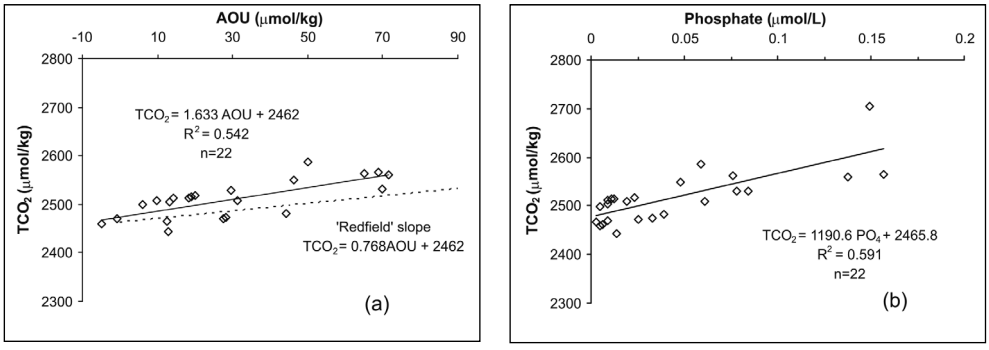

Fig. 4: TCO_2 *vs.* (a) AOU and (b) phosphate for the samples from the last depth of the TP- and M-stations.

ments, and which can affect the nitrogen to carbon balance. The relatively good correlation between TCO_2 and phosphate (r^2=0.591) indicates that in the close to the bottom layer of the Thermaikos Gulf a large proportion of both parameters originates from the remineralisation of organic matter. However, there is more carbon and less phosphorus regenerated than the amounts predicted from the oceanic model (almost 10 times). The composition of the organic matter that is remineralised -particularly rich in carbon in relation to phosphorus- could be a possible reason for the value of the ratio.

During May 1997, both the estimated oxygen consumption and phosphate and carbon regeneration rates in the Thermaikos Gulf are considerably higher in relation to the open ocean estimates, indicating an excess in TCO_2, and/or a deficit in AOU and phosphate and should probably be attributed to the proximity of the study area to the coastal zone and/or to the quantity and quality of the organic matter that is remineralised.

The fugacity of CO_2 in seawater (fCO_2)

The main factors controlling the variation of sea surface fCO_2 in the open ocean are the warming and cooling of surface waters (temperature), and the balance between photosynthetic carbon fixation and release of CO_2 by respiration or oxidation of organic matter. In coastal seas the same processes take place, yet with more intensity and variability. One common aspect of the coastal CO_2 studies is the large variability of fCO_2 measured in surface waters, significantly greater in both space and time than typically observed in open ocean environments.

In the Thermaikos Gulf during May 1997 the surface fCO_2 varied between 273 µatm (TP01) and 383 µatm (TP16), while the surface temperature ranged between 13.9 (TP13) and 18.3 °C (TP01). In the greater part of the gulf the fCO_2 values (Fig. 5) are lower (average: 332 µatm) than the present atmospheric annual mean value of about 365 µatm (CHAMARD *et al.,* 2001), the surface

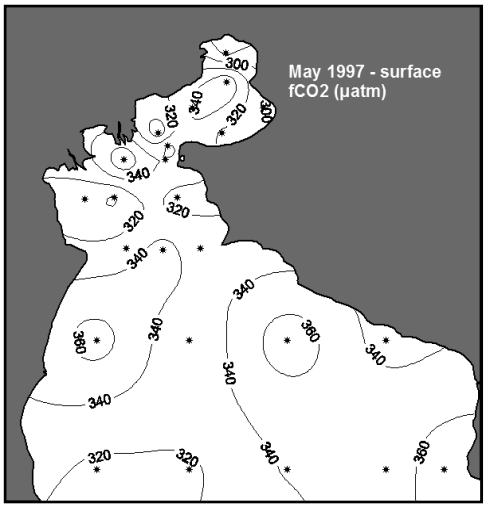

Fig. 5: Surface distribution of fCO_2^w in the Thermaikos Gulf during May 1997.

waters of the Thermaikos appear undersaturated with respect to the atmosphere and the region could act as a sink for atmospheric CO_2.

Temperature affects the equilibrium constants of inorganic carbon and particularly the solubility coefficient of CO_2; heating decreases the solubility of CO_2 and increases the fugacity of CO_2 in seawater (e.g. for a temperature increase of 1 °C, pCO_2 rises ~4%), which may induce CO_2 oversaturation in many cases and a CO_2 source to the atmosphere. The fCO_2 data are normalised to a fixed temperature of 16 °C (fCO_2^T), representing the mean surface water temperature during the cruise, in order to eliminate the thermodynamic effect on fCO_2. Model II regressions were calculated between the temperature-normalised fugacity data and chlorophyll α, temperature and AOU in order to analyse the factors behind the fCO_2 variability.

The correlation between chlorophyll α and fCO_2^T is negative (Fig. 6a); the maximum fCO_2^T values were recorded in the southern part of the gulf where the phytoplanktonic biomass was low. The minimum fCO_2^T coincides with the maximum concentration of

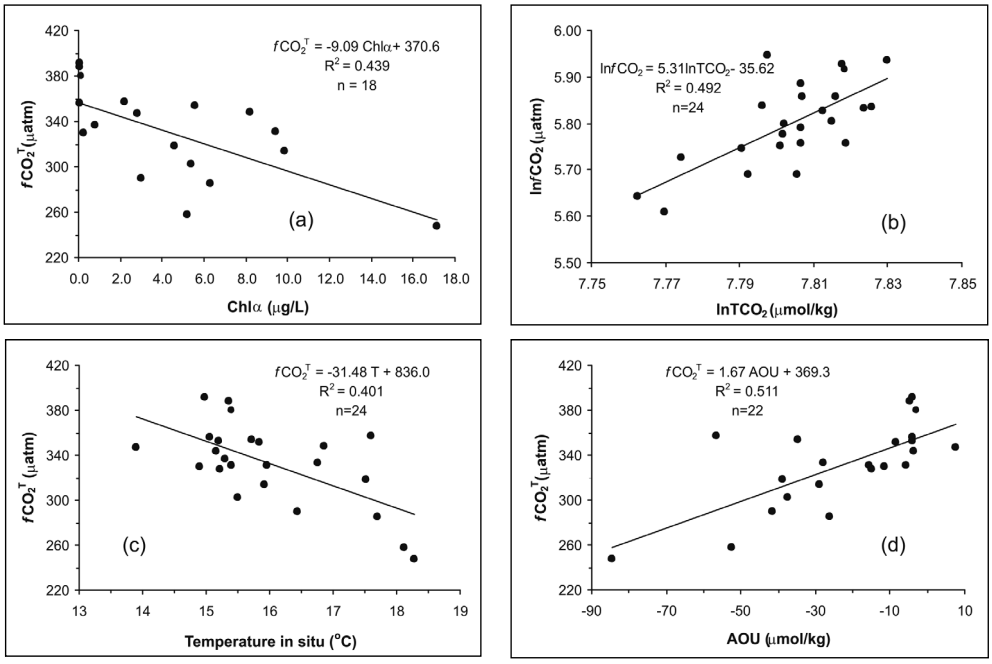

Fig. 6: Plots and Model II regressions of (a) fCO_2^T *vs.* chlorophyll *a*, (b) lnfCO_2 vs. lnTCO_2 (c) fCO_2^T *vs* surface temperature and (d) fCO_2^T *vs* AOU in the Thermaikos Gulf during May 1997.

chlorophyll *α* in the innermost part of the gulf, where biological activity leads to the draw down of CO_2 and thus strongly reduces fCO_2^T levels. Moreover, the dynamics of inorganic carbon resulting from photosynthesis are highly dependent upon the types of organisms present and whether they are calcifying or not. Photosynthesis and calcification have opposing effects on the fCO_2 and the final result of their concomitance depends on their relative importance. A convenient parameter to study the importance of calcification, the homogenous buffer factor β, which is defined as the relative variation of the fCO_2 to that of TCO_2 ($\beta = \partial \ln fCO_2 / \partial \ln TCO_2$), was also employed. The factor β ranges from ~12, when no calcification occurs during organic matter production to about -7, when precipitation/dissolution of $CaCO_3$ is the only occurring process (FRANKIGNOULLE, 1994). The calculated β value of 5.31 (Fig. 6b) indicates that calcification or carbonate dissolution takes place on a very small scale, simultaneously with organic carbon production, in agreement with the comparatively conservative character of TA (section 3.2).

In addition, the fCO_2^T drastically decreases instead of increasing as expected from the temperature increase and shows a moderate negative correlation with temperature (Fig. 6c). This fact arises from a correlation between warm waters of low fCO_2 with cold waters of high fCO_2 levels and suggests that the spatial variability of fCO_2^T is mainly driven by photosynthetic activity, which seems to overwhelm the expected variability due to temperature differences.

The negative AOU values (i.e. oxygen production) over the whole study area and the positive correlation between AOU and fCO_2^T (Fig. 6d) strengthens the view that the principal factor that modulates fCO_2^T variability is primary productivity.

Air-sea CO_2 exchanges

A concentration difference of carbon di-

oxide (CO_2) across the air-water interface drives the net gas exchange. A common assumption is that a concentration gradient of CO_2 exists only near the air-water interface and that the gas is well mixed in bulk air and bulk water.

Air-sea exchange slowly brings the concentration of dissolved CO_2 in surface water towards an equilibrium with the atmospheric CO_2 content. More rapid physical and biological disturbances of the concentration of CO_2 in water generally prevent this equilibrium from being established.

The net flux of CO_2 through the air-sea interface (F_{CO2}, mmol m^{-2} d^{-1}) is described as:

$$F_{CO2} = K_w \text{ X } S \text{ X } (fCO_2^w - fCO_2^a) \qquad (1)$$

where K_w (cm h^{-1}) is the gas transfer coefficient, S (mol L^{-1} atm^{-1}) is the solubility of CO_2 in seawater, and fCO_2^w and fCO_2^a (µatm) are the fugacity of CO_2 in seawater and air, respectively. Several parameterizations of K_w have been proposed based on laboratory and field studies, taking into account a wide variety of factors affecting air-sea exchange: wind, bubbles, turbulence, temperature, atmospheric boundary layer stability, and drag coefficients (SMETHIE *et al.,* 1985; LISS & MERLIVAT, 1986; WOOLF, 1997; TANS *et al.,* 1990; WANNINKHOF, 1992; WANNINKHOF & MCGILLIS, 1999; Mc GILLIS *et al.,* 2001). In our calculations, we use the K_w-wind speed algorithms proposed by LISS & MERLIVAT (1986), WANNINKHOF (1992), WANNINKHOF & Mc GILLIS (1999) and Mc GILLIS *et al.,* (2001), hereafter referred to as LM86, W92, WMG99 and MG01, respectively. In fact, it is difficult to choose one relationship because even the latest experiments using the most recent tracer techniques could not reliably distinguish which was the more favourable relationship. In addition, the fluxes reported in the literature are usually computed using only one of the above mentioned relationships and thus, for comparative reasons, it is useful to have the values calculated using the various relationships. We, therefore, chose to report the results computed with the different formulations.

To evaluate the air-sea CO_2 exchanges, the fCO_2^a must be known. However, during this study atmospheric measurements were not performed. The spatio-temporal variability of the atmospheric molar fraction of CO_2 (xCO_2^a) is much smaller than that of seawater (xCO_2^w), mainly because of the high lateral atmospheric mixing rates, which tend to rapidly homogenize xCO_2^a. Therefore, we can compute the flux of CO_2 across the air-sea interface, assuming a constant atmospheric fCO_2 during the cruise, using the values of atmospheric fCO_2^a from Lampedusa Island in the central Mediterranean Sea, which is the nearest marine site of atmospheric CO_2 monitoring to the Thermaikos Gulf (CHAMARD *et al.,* 2001).

Wind speed data for the period of our observations were obtained from the ECMWF MARS database and correspond to the available measurements from the meteorological station located at Thessaloniki airport (40.517N 22.967E); however, wind speed measurements of a higher resolution, both temporally and spatially, are likely to be necessary in order to estimate more realistically the air-sea CO_2 exchanges. The data from an onboard meteorological station would be most appropriate to calculate the gas transfer coefficient; nevertheless, through the use of the available data, both of fCO_2^a and wind speed, a rough first assessment of the role of the Thermaikos Gulf in air-sea CO_2 exchange can be obtained.

This simplistic approach to calculating the air-sea CO_2 flux involves several major assumptions, but the approximate magnitude and the relative role of the Thermaikos Gulf in the uptake or release of atmospheric CO_2 can be determined.

The results of the four formulations show that during May 1997 the net flux of CO_2 through the air-sea interface is negative and the whole Thermaikos Gulf absorbs atmos-

pheric CO_2 at a rate between -0.60 and -1.43 mmol m^{-2} d^{-1}, depending on which gas transfer coefficient is used (Table 1). The obtained results are in agreement with the direction of the CO_2 fluxes reported in other temperate continental shelf areas. Existing data on air-sea CO_2 fluxes suggest that temperate marginal seas act as sinks for atmospheric CO_2 (e.g. East China Sea, TSUNOGAI *et al.,* 1999; Gulf of Biscay, FRANKIGNOULLE & BORGES, 2001; US Middle Atlantic Bight, DEGRANDPRE *et al.,* 2002; RIA DE VIGO, NW Spain, GAGO *et al.,* 2003; North Sea, BOZEC *et al.,* 2005). Comparing the magnitude of the fluxes to the data from other coastal seas during spring-summer (Table 1), our study shows that the Thermaikos Gulf acted as a weak sink for atmospheric CO_2 during May 1997.

During winter, higher gas transfer velocities are expected due to the usual increase in wind force; this higher wintertime transfer of carbon dioxide is also provoked by the temperature decrease of surface waters, which drives a decrease of fCO_2^w values and enhances the penetration of atmospheric CO_2. In addition, the dense water formed due to the water cooling in the shallow northern part of the gulf (KONTOYIANNIS *et al.,* 2003) and the subsequent slow spreading and mixing transports this enriched in dissolved inorganic carbon water into the deeper layer of the outer gulf. Therefore, it is quite possible that during winter the Thermaikos Gulf could be a more effective CO_2 sink than in late spring. This scenario is likened to the 'continental shelf pump' that has been employed recently by TSUNOGAI *et al.,* (1999) to explain the observed large net absorption of CO_2 in the East China Sea during winter.

Table 1

Air-sea CO_2 fluxes calculated using different gas transfer coefficients for the Thermaikos Gulf during May 1997 and other representative temperate continental seas during spring-summer.

Thermaikos gulf	
Range of fCO_2^w (μatm)	273 -383
Range of ΔfCO_2 (μatm)	-92.5 - 17.6
Average of ΔfCO_2 (μatm)	-33.5
Average wind speed (m s^{-1})	4.6
$F_{CO2} \pm \sigma$ (mmol m^{-2} d^{-1}) - LM86	-0.72 ± 0.42
$F_{CO2} \pm \sigma$ (mmol m^{-2} d^{-1}) - W92	-1.43 ± 0.84
$F_{CO2} \pm \sigma$ (mmol m^{-2} d^{-1}) - WMG99	-0.60 ± 0.35
$F_{CO2} \pm \sigma$ (mmol m^{-2} d^{-1}) - MG01	-1.35 ± 0.79
Other continental seas	
North Sea F_{CO2} (mmol m^{-2} d^{-1}) - LM86[1]	-2.1 - -1.5
North Sea F_{CO2} (mmol m^{-2} d^{-1}) - W92[1]	-3.4 - -1.6
North Sea F_{CO2} (mmol m^{-2} d^{-1}) - WMG99[1]	-1.8
Baltic Sea F_{CO2} (mmol m^{-2} d^{-1}) - W92[2]	-6.4
Ria de Vigo F_{CO2} (mmol m^{-2} d^{-1}) - LM86[3]	-1.31 - 0.39
East China Sea F_{CO2} (mmol m^{-2} d^{-1}) - LM86[4]	-3.3 - -1.8
East China Sea (mmol m^{-2} d^{-1}) - W92[4]	-6.5 - -4.7

[1] BOZEC *et al.* (2005); [2] THOMAS & SHNEIDER (1999); [3] GAGO *et al.* (2003); [4] WANG *et al.* (2000).

Conclusions

The present study enabled us to describe the distribution of dissolved inorganic carbon and related parameters in the Thermaikos Gulf waters during May 1997. Surface concentrations of TCO_2 were lower than those recorded close to the bottom. The decomposition of the organic material, imported directly from external sources (rivers, sewage) and produced *in situ* in the Thermaikos, resulted in an increase of the concentration of dissolved inorganic carbon, particularly in bottom layer. The positive relatively good correlation between TCO_2 and both AOU and phosphate at the last sampling depth confirmed the regenerative origin of a large proportion of TCO_2. The correlations between surface fCO_2, calculated from the TA and TCO_2 measurements, and chlorophyll α as well as AOU revealed that the carbon dioxide fixation through biological activity was the principal factor modulating the variability of fCO_2.

Moreover, a simplistic first estimate of the role of the Thermaikos Gulf in air-sea CO_2 exchange was obtained. The results showed that during May 1997, the Thermaikos Gulf acted as a weak sink for the atmospheric CO_2 at a rate of -0.60 - -1.43 mmol m^{-2} d^{-1}, depending on which formula for the gas transfer velocity was used.

Extensive study of the dissolved inorganic carbon and related parameters, continuous shipboard measurements of fCO_2^a and fCO_2^w during all seasons would be necessary to safely quantify the role of the Thermaikos Gulf in the context of the coastal margins CO_2 dynamics. Simultaneous measurements of the *in situ* processes affecting the dissolved inorganic carbon system may yield a better understanding of the mechanisms involved.

Aknowledgements

This work was supported by the EU MAST-III ELOISE Project METRO-MED (Dynamics of Matter Transfer and Biogeochemical Cycles: Their Modelling in Coastal Systems of the Mediterranean Sea), contract MAS3-CT96-0049. We wish to thank Dr A. Papadopoulos for providing the wind data from the EMCWF database and Dr K.Pagou and G. Assimakopoulou for the chlorophyll α data.

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Accepted in March 2007