Partial pressure and air–sea CO₂ flux in the Aegean Sea during February 2006

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ABSTRACT

Data on the distribution of fCO₂ were obtained during a cruise in the Aegean Sea during February 2006. The fCO₂ of surface water (fCO₂sw) was lower than the atmospheric fCO₂ (fCO₂atm) throughout the area surveyed and ΔfCO₂ values varied from −34 to −61 μatm. The observed under-saturation suggests that surface waters in the Aegean represent a sink for atmospheric CO₂ during the winter of 2006. Higher fCO₂sw values were recorded in the ‘less warm’ and ‘less saline’ shallow northernmost part of the Aegean implying that the lower seawater temperature and salinity in this area play a crucial role in the spatial distribution of fCO₂sw.

A first estimate of the magnitude of the air–sea CO₂ exchange and the potential role of the Aegean Sea in the transfer of atmospheric CO₂ was also obtained. The air–sea CO₂ fluxes calculated using different gas transfer formulations showed that during February 2006, the Aegean Sea absorbs atmospheric CO₂ at a rate ranging from −6.2 to −11.8 mmol m⁻² d⁻¹ with the shipboard recorded wind speeds and at almost half rate (−3.5 to −5.5 mmol m⁻² d⁻¹) with the monthly mean model-derived wind speed. Compared to recent observations from other temperate continental shelves during winter period, the Aegean Sea acts as a moderate to rather strong sink for atmospheric CO₂.

Further investigations, including intensive spatial and temporal high-resolution observations, are necessary to elucidate the role of the Aegean Sea in the process of transfer of atmospheric CO₂ into the deep horizons of the Eastern Mediterranean.

1. Introduction

The number of measurements of the partial pressure of CO₂ (pCO₂) in the world ocean has increased considerably during the past two decades. Despite the wide scope and enlightening results of these studies, they have chiefly focused on the open oceans. At present it is difficult to assess the source/sink terms and the associated air–sea CO₂ fluxes of the global ocean margin due primarily to the lack of pCO₂ field data with high spatial and temporal resolution in these heterogeneous and dynamic environments. Only recently have marginal seas received attention, albeit still very limited. Available data indicate that marginal seas in high and temperate latitudes may act as sinks of atmospheric CO₂ while subtropical and tropical marginal seas, estuaries and coral reefs, in general, act as sources (Borges, 2005 and references therein; Borges et al., 2006 and references therein).

The Mediterranean Sea, a semi-enclosed basin of about 2.5 million km² and 1.5 km average water depth, still primarily remains a mostly unexplored territory in spite of the few recently published data associated with the air–sea exchange of CO₂, which are spatially restricted in the western basin (Copin-Montegut, 2000; Hood and Merlivat, 2001; Bégovic and Copin-Montégut, 2002; Copin-Montégut et al., 2004) and the Gibraltar strait (Ait-Amour and Goyet, 2006). Recently, Krasakopoulou et al. (2007) reported that the Thermaikos Gulf (Eastern Mediterranean-NW Aegean Sea) acts as weak sink of atmospheric CO₂, based on calculated fCO₂ values from dissolved inorganic carbon and total alkalinity data collected during May 1997.

Basin-scale estimates of the CO₂ air–sea flux in the Mediterranean have been produced by indirect methods, as a residual after all other terms of the carbon budget are determined (Copin-Montegut, 1993), as well as by extrapolation of the annual flux calculated at the DyFAMed station over the whole Mediterranean Sea surface (Hood and Merlivat, 2001). In particular, Copin-Montegut (1993) determined a weak sink for the atmospheric CO₂ with a climatological integrated flux of 0.35–1.85 x 10¹² mol y⁻¹. A large uncertainty, however, is attached to the magnitude and direction of this flux. Based on time series of
$f_{\text{CO}_2}$ data collected between 1995 and 1997 by a CARIOCA buoy at the DyFAMed station, Hood and Merlivat (2001) calculated an annual transfer rate between $-0.10$ and $-0.15 \text{ mol CO}_2 \text{ m}^{-2} \text{ y}^{-1}$, using the Liss and Merlivat (1986) or Wanninkhof (1992) gas transfer formulation, respectively. Extrapolating this rate over the surface area of the Mediterranean Sea ($2.5 \times 10^{12} \text{ m}^2$) yielded a flux between $-2.5 \times 10^{11}$ and $-3.8 \times 10^{11} \text{ mol CO}_2 \text{ y}^{-1}$. Very recently D’Ortenzio et al. (2008), based on satellite-driven modelling of the upper mixed layer, provided a detailed analysis of the seasonal distribution of $p_{\text{CO}_2}$ in the Mediterranean Sea and estimated that the Mediterranean is close to equilibrium with the atmosphere with, however, a small sink for the atmospheric $\text{CO}_2$, in coherence with previous studies. Their analysis revealed important differences between the eastern and the western Mediterranean basins: the ultra-oligotrophic Eastern Mediterranean is oversaturated in $\text{CO}_2$ for most of the year, while the spring phytoplankton blooms significantly contribute to the under-saturation of the western Mediterranean surface layers.

In this study, the first $x_{\text{CO}_2}$ records in the Aegean Sea (Eastern Mediterranean) based on continuous measurements are presented and provide an important case study on the role of the Aegean Sea as source or sink of atmospheric $\text{CO}_2$.

### 2. Materials and methods

#### 2.1. Study area

The Aegean Sea is a distinct sub-system of the Eastern Mediterranean Sea due to its geographical position between the Black Sea and the other seas of the eastern basin (Ionian and Levantine Seas). The bottom topography of the region is characterised by an alternation of plateaux and deep troughs: the Cyclades plateau separates the North from the South Aegean basins, allowing water exchange above 400-m depth. Below 400 m, the deep basins of the North Aegean are filled with very dense water of local origin (Zervakis et al., 2000) and the deep basin of the South Aegean with Cretan Deep Water (Theocharis et al., 1999). The general circulation within the Aegean Sea is cyclonic (Fig. 2): highly saline ($S > 38.8 \text{ psu}$) and warm ($16–25 ^\circ \text{C}$) water of Levantine origin, dominant in the South Aegean, travels northwards along the western coast of Turkey (Theocharis et al., 1999). A surface layer of very light, brackish ($S \sim 30 \text{ psu}$) and cold ($9–22 ^\circ \text{C}$) water is formed in the northeast Aegean by the inflow of modified Black Sea Water (BSW) through the Dardanelles straits affecting the uppermost (20–30 m) layer of the North Aegean Sea and is modified moving westward and southward by lateral and...
diapycnal mixing with the waters of Levantine origin. The latter, being diluted to salinities of about 38 psu by the overlying BSW in the North Aegean, flows southwards along the eastern coast of the Hellenic peninsula, eventually entering the South Aegean and the Cretan basin (Zervakis et al., 2005). The different hydrographic conditions prevailing in the North and South Aegean Sea due to the influence of Black Sea and of Levantine origin waters, respectively, greatly affect the biogeochemical processes and dynamics. Although the Aegean Sea has been characterised as an overall oligotrophic environment, it exhibits significant trophic spatial variability. This differentiation both in terms of biomass and production is expressed along a gradient of oligotrophy from the northeast Aegean Sea, which is influenced by the BSW, towards the South Aegean Sea (Siokou-Frangou et al., 2002 and references therein). Higher chlorophyll-a (chl-a), phytoplankton and zooplankton abundance, primary production and bacteria production levels were observed in the North than in the South Aegean Sea, which is considered as “typical oceanic margin” environment (Lykousis et al., 2002). Previous studies in the Aegean have shown that maximum values of phytoplankton biomass (chl-a) and primary production are recorded mostly in late winter and spring, attributed to relatively high nutrient concentrations, whereas minimum values occur in summer-autumn (Ignatiades et al., 2002). Coccolithophores are the dominant phytoplankton group producing carbonate in the area (Ignatiades et al., 2002; Dimiza et al., 2008).

2.2. Sampling

Continuous measurements of atmospheric and dissolved CO₂ were performed in the Aegean Sea during February 2006 (8–13/2/2006) onboard the R/V Aegeo. The cruise track was an almost N-S latitudinal transect along the Aegean, covered the central Cretan Sea and passing through the Myrtoan Sea, ending at Piraeus (Fig. 1).

Seawater was pumped continuously from the bow intake located 2.0 m below the sea surface, using the ship’s water pump system and was sprayed into a Weiss equilibrator at 12–15 L min⁻¹. The basic operational and physical principles of this equilibrator are described elsewhere (Weiss et al., 1992; Johnson, 1999). Two pressure-equilibrating tubing lines in the equilibrator ensured sampling under atmospheric pressure, hence no pressure correction had to be applied (Fig. 2).

Ambient air was pumped continuously with a flow of 1.3 L min⁻¹ through approximately 30 m long polypropylene tubing from the ship’s bow 6 m above sea level into the Laboratory. The carbon dioxide content of the headspace of the equilibrator and of the marine air was measured with an automated gas chromatograph (Shimadzu GC/FID) where the CO₂ is catalytically reduced to methane, which is detected by a flame-ionisation detector (FID) (Weiss, 1981). Briefly, the analysis was performed isothermally on a mol sieve 5 Å column at 55 °C, with an injector temperature of 300 °C and a detector temperature of 280 °C. A 10-port valve with two sample loops was used to inject the sample, which was dried before entering the analytical system by means of a 30-cm glass tube filled with Sicapent drying agent. Sampling alternated between ambient air and equilibrated air. Two CO₂ standards of 257 and 345 ppmV CO₂ provided from Messer-Griesheim were used to calibrate the system during the cruise. The reproducibility (1σ) of the measurements was less than ±0.4 ppmV as determined from multiple injections of the calibration gases. The sequence of measurements was set to produce two successive readings of equilibrator gas followed by two successive readings of air sample (20 min each cycle). The duplicate readings from two different sample loops provided us with the confidence that the possible significant local variations in CO₂ concentrations were more than accurate. The accuracy of the entire system was better than 0.5 ppmV for xCO₂ atm and 1.0 ppmV for xCO₂ sw.

Salinity and seawater temperature were measured continuously using a permanently installed SeaBird SBE 21 CTD probe. Temperature and salinity readings were calibrated against the measurements performed during the CTD stations. Meteorological parameters (air temperature, relative humidity, atmospheric pressure, wind direction and wind speed) were recorded every 30 s by the automated Aanderaa weather station located close to the bridge of the ship, at about 10 m above sea level. Wind data were corrected for ship’s movements, based on concurrent data on ship’s velocity and heading. To remove the effects of small-scale turbulent fluctuations, the onboard wind speed records have been averaged over a 20-min period in accordance with the xCO₂ data recording cycles. Quality control has been applied to remove erroneous wind data, based on checking the physical range (0–28 m s⁻¹), the allowable rate of change in time (an observation is omitted if its difference from the previous and next ones exceeds 5 m s⁻¹) and the stationarity (wind speed is not allowed to be constant for a period more than 2 h).

2.3. Calculation of fugacity

The gas chromatographic analysis provides the molar fraction of CO₂ in dry air (xCO₂) which then is converted into CO₂ fugacity (fCO₂). Since CO₂ is a non-ideal gas the correct way of expressing
the thermodynamic driving force of gas flux is in terms of fugacity than of partial pressure (Weiss, 1974). For ambient air, assuming 100% water vapour saturation, the $f_{\text{CO}_2}^{\text{atm}}$ is calculated according to:

$$f_{\text{CO}_2}^{\text{atm}} = x_{\text{CO}_2}^{\text{atm}}(p - p_{\text{H}_2\text{O}})\exp[(B_{11} + 2\delta_{12})p/RT]$$

where $p_{\text{H}_2\text{O}}$ is the water vapour pressure at the sea surface temperature, and $p$ is the atmospheric pressure measured by the ship-based meteorological sensor. The exponential term is the fugacity correction where $B_{11}$ is the second virial coefficient for pure $\text{CO}_2$, $\delta_{12}$ is the correction for an air-$\text{CO}_2$ mixture (Weiss, 1974), $R$ is the gas constant and $T$ is the absolute temperature. The calculation of the fugacity in surface seawater ($f_{\text{CO}_2}$) includes the empirical temperature correction for $f_{\text{CO}_2}$ proposed by Takahashi et al. (1993) (i.e. $f_{\text{CO}_2} = f_{\text{CO}_2}^{\text{9} C}$) due to the heating of the seawater when passing through the pump and the tubing within the ship. The temperature increase of seawater in the equilibrator was generally less than 0.5°C, compared to sea surface temperature, and would cause an increase of $f_{\text{CO}_2}$ values of about 2%. The fugacity in seawater is calculated according to:

$$f_{\text{CO}_2}^{\text{sw}} = x_{\text{CO}_2}^{\text{sw}}(p - p_{\text{H}_2\text{O}_\text{eq}})\exp[(B_{11} + 2\delta_{12})p/RT] \times \exp(f_{\text{sw}} - f_{\text{atm}}0.0423)$$

2.4. Calculation of the air–sea $\text{CO}_2$ fluxes

The $\text{CO}_2$ flux ($F_{\text{CO}_2}$, mmol m$^{-2}$ d$^{-1}$) across the air–sea interface can be computed from the sea–air gradient of $f_{\text{CO}_2}$ ($\Delta f_{\text{CO}_2} = f_{\text{CO}_2}^{\text{sw}} - f_{\text{CO}_2}^{\text{atm}}$, µatm), the solubility coefficient $K_s$ of $\text{CO}_2$ in seawater (mol L$^{-1}$ atm$^{-1}$), which depends on temperature and salinity (Weiss, 1974) and the gas transfer velocity $k$ (cm h$^{-1}$) according to: $F_{\text{CO}_2} = K_s \times \Delta f_{\text{CO}_2}$. The difference between $f_{\text{CO}_2}^{\text{sw}}$ and $f_{\text{CO}_2}^{\text{atm}}$ determines the direction of the exchange and $k$ controls the transfer rate. The above parameterisation implies that fluxes at the air–sea interface into the surface water are denoted with a negative sign, whereas fluxes into the atmosphere are denoted by a positive sign. Several algorithms for the $k$-wind speed relationship have been proposed based on laboratory and field studies, taking into account a wide variety of factors affecting air–sea exchange: wind speed, bubbles, turbulence, temperature, atmospheric boundary layer stability and naturally occurring surfactants (Upstill-Goddard, 2006 and references therein).

The Liss and Merlivat (1986) and the Wanninkhof and McGillis (1992) parameterisations of the dependency of the transfer velocity $k$ on wind speed $u$, hereafter referred to as LM86 and W92, respectively, are quadratic or near-quadratic; W92, for example, parameterises $k$ as a function of $u$ as $k = 0.3u_{10}(S/660)^{-0.5}$, where $S$ is the Schmidt number of $\text{CO}_2$ in seawater, 660 is the $S$ for $\text{CO}_2$ in seawater at 20°C and $u_{10}$ is the wind speed corrected to 10 m height under neutral conditions. Recent work, based to a large extent on measurements performed during the GasEx-1998 field experiments (McGillis et al., 2004), has resulted in other cubic parameterisations, which yield better fits to the data (e.g. Hare et al., 2004 and references therein). Wanninkhof and McGillis (1999), using laboratory and field studies, proposed a cubic relationship between air–sea gas exchange and wind speed, $k_{660} = 0.028u_{10}$, or $k = 0.228u_{10}(S/660)^{-0.5}$, which, compared with previous calculations using the W92 parameterisation, resulted in a significant increase in the calculated oceanic global annual $\text{CO}_2$ uptake. Fairall et al. (2000) reviewed the theoretical basis of various parameterisation schemes for bulk-to-bulk gas transfer. Since then, McGillis et al. (2001) used eddy accumulation for $\text{CO}_2$ to determine $k$ and showed that $k$ can be described as $k_{660} = 3.3 + 0.026u_{10}$, where $k_{660}$ is the $k$ normalised to $S$ of 660 in cm h$^{-1}$ (which equals the $S$ for $\text{CO}_2$ in seawater at 20°C). Wanninkhof et al. (2004) during the Southern Ocean Iron Fertilisation Experiment (SOFex) used measurements of dual tracers, addressing the discrepancies between observational and model-based estimates of $\text{CO}_2$ uptake in the Southern Ocean (see also Feely et al., 2004). Work on the same experiment also considered the effect of wind speed products ( Olsen et al., 2005) and addressed the effects of sea-state–dependent wave breaking (Woolf, 2005).

In the present study, for comparative purposes with other studies, the $k$-wind speed parameterisations of LM86, W92 and additionally, the more recent parameterisations of Wanninkhof and McGillis (1999) and McGillis et al. (2001), hereafter referred to as WMC99 and MG01, respectively, were applied to determine the $\text{CO}_2$ flux across the sea–air interface using cruise data. LM86, W92 and MG01 normalise their parameterisations with respect to the $S$ of $\text{CO}_2$ in seawater at 20°C. Also, we note here that while LM86 note 600 as the $S$, of $\text{CO}_2$ at 20°C, W92 and MG01 note 660 as the $S$, of $\text{CO}_2$ at 20°C. However, $k$ being a function of either $(S/600)^{-0.5}$ or $(S/660)^{-0.5}$, the error in the values of $k$ from this convention is less than 5%.

3. Results and discussion

3.1. Meteorology and hydrography

Between 8 and 13 February 2006 very bad weather conditions prevailed over the Aegean; a low pressure system developed and influenced the meteorological conditions, air temperatures ranged between 1.1 and 15.1°C, strong and cold winds blew mainly from a N-NE direction with velocities reaching 17 m s$^{-1}$ (Figs. 3 and 4). The extremely strong winds (13–17 m s$^{-1}$) when sampling the Cyclades Plateau lead to the cancellation of the field work for about 24 h (from the morning of 10/2 till the morning of 11/2/2006).

Sea surface temperature and salinity records obtained during the cruise are presented in Fig. 5, plotted using Ocean Data View (ODV; Schlitzer, 2009). The northernmost edge of the cruise track is characterised by the lowest temperature and salinity values (10.1°C and 36.3, respectively). The presence of this low temperature and salinity water mass is attributed to the inflow of modified BSW through the Dardanelles straits as well as to the advection of fresh waters from the rivers discharging in the northern coast of Greece. In general, during the cruise the minimum and maximum values of seawater temperature follow the same latitudinal distribution pattern and coincide with the minimum and maximum values of air temperature (not shown). South of 39 30’N temperature and salinity increase steadily.

![Fig. 3. Time evolution of air temperature and atmospheric pressure in the Aegean Sea in the period between 8 and 13 February 2006.](image-url)
indicating the mixing of BSW with warmer and saltier waters of Levantine origin. The Levantine waters during their northward journey along the eastern Aegean have undergone high amounts of evaporation and become saltier, as well as losing heat into the atmosphere and becoming colder. The most saline and warmest surface waters were detected during 10/2/06 in the north of Ikaria island. Colder and less saline waters are detected west of 24°E and north of 37°N, probably related to the presence of modified BSW.
transported in the area by a small part of the current that flows south-eastward along the eastern coast of Evvoia island and then flows south-westward to enter the Myrtoan Sea, in agreement to the general circulation of the Aegean (Fig. 2).

3.2. Distribution of fCO2 and relationships with seawater properties

The xCO2 data recorded during the cruise allow us to plot the first map of fCO2sw for the Aegean Sea in winter (Fig. 6). The average surface water fCO2 was 323 ± 5 μatm and ranged between 312 and 338 μatm. By comparison, atmospheric fCO2 ranged between 361 and 380 μatm having an average value of 369 ± 4 μatm. The fCO2 of surface water of the entire survey area was lower than the atmospheric fCO2 suggesting thus undersaturation of surface waters with respect to the overlying atmosphere. This under-saturation leads to ΔfCO2 values from −34 to more than −60 μatm, and hence surface waters in the Aegean represent a sink for atmospheric CO2 during winter 2006. The saturation state of the surface waters expressed by the saturation ratio, SR (SR = (Csw/Catm) × 100, where Csw and Catm are the gas concentrations of the seawater and the calculated concentration in equilibrium with ambient atmospheric partial pressure, respectively) was higher than 80% and ranged between 83% and 90%.

Based on the slightly different levels of the fCO2sw in the surface waters that were observed (Fig. 6), the Aegean Sea can be separated into three regions: (a) north of 39.45°N, namely the northeastern Aegean, with fCO2sw values ranging between 328 and 338 μatm (average ± std. dev.: 331 ± 4 μatm), (b) between 39.30°N and 36.45°N that comprises the central Aegean, Cyclades Plateau and Myrtoan Sea, characterised by lower fCO2sw values (average ± std. dev.: 323 ± 4 μatm) and (c) south of 36.45°N namely the Cretan Sea, with somewhat lower fCO2sw levels (average ± std. dev.: 320 ± 5 μatm).

The fCO2 of surface seawater is controlled by the following processes: thermodynamical change, air–sea exchange, biological activity and mixing processes. The temperature effect on fCO2sw is opposite in direction to the biological production; temperature increases lead to higher fCO2sw, whereas photosynthetic activity leads to drawdown of CO2 and thus fCO2sw decreases. Generally, a great part of the fCO2sw variations are due to the temperature dependence of the carbonate equilibria. These functional variations of fCO2sw with temperature may obscure the correlation with the other variables. In order to eliminate the thermodynamic effect on fCO2sw, the fCO2sw data are normalised to a fixed temperature of 14.9 °C (NfCO2sw), representing the mean surface water temperature during the cruise, using the empirical equation of Takahashi et al. (1993).

Since the temperature effect has been removed, changes in fCO2sw would reflect primarily the influence of the invasion and evasion of atmospheric CO2, biological uptake or production of CO2 and mixing with other water masses.

Fig. 7 shows the correlations of the temperature normalised fCO2sw (NfCO2sw) with other measured variables (surface seawater temperature, salinity, wind speed), as well as the fCO2sw-temperature relationship and the T–S diagram.

The NfCO2sw was higher in the shallow northernmost part of the Aegean where the salinity is lower than 38.5 and temperature lower than 13.5 °C (Fig. 7b and c). The NfCO2sw drastically decreases instead of increasing as expected from the temperature increase and shows a strong negative correlation with temperature (Fig. 7b). This fact arises from a correlation between warm waters of lower fCO2 and cold waters of higher fCO2sw. The invasion of atmospheric CO2 into the upper layer of the northeast Aegean as a result of surface cooling is the process that probably contributes to the observed higher fCO2sw values. In these shallow shelf waters the cooling is greater than for the nearby open waters. Consequently, it is possible that the strong solubility pump leads to strong CO2 under-saturation which then results in an intensified uptake of atmospheric CO2 on the continental shelf. The presence of low salinity waters could also contribute to the occurrence of the elevated fCO2sw values in the northeast Aegean. Although any other parameter of the CO2–carbonate system was not measured on this cruise, pH and fCO2sw values calculated from dissolved inorganic carbon and total alkalinity data collected in the Aegean in September 2005 and April 2006 are generally consistent with the present observations, i.e. lower pH values generally coincide with lower salinity and higher fCO2sw values (Triantaphyllou et al., 2009).

Fig. 7c shows the dependency of the temperature normalised fCO2sw data on salinity and reveals that surface waters having almost the same salinity may be characterised by different NfCO2sw values. It is interesting to note that although the temperature effect was removed, the signal of the different waters remains on the NfCO2sw. Hence the NfCO2sw versus salinity diagram matches well with the T–S diagram (Fig. 7d), where the surface waters of the eastern Cretan Sea with mean salinity ~38.8 have almost the same temperature and NfCO2sw values as that of the surface waters of the Cyclades Plateau and of the area in the vicinity of Ikaria island, which are characterised by a mean salinity >39.0.

From Fig. 7e it is obvious that wind speed does not affect the NfCO2sw levels. It is assumed that high wind speeds or rapid wind speed changes did not cause rapid changes in surface water fCO2sw, as a result of the strong buffering of ocean CO2 with respect to gas exchange.

The lack of chl-a data, as well as of continuous fluorescence records during the cruise, led us to use the chl-a distribution

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**Fig. 6.** Spatial distribution of fCO2sw (μatm) in the surface waters of the Aegean Sea during 8–13 February 2006.
based on weekly averaged Moderate Resolution Imaging Spectroradiometer data (MODIS—4 km resolution) for the time period of the cruise (Fig. 8). The elevated chl-a values (up to 4.5 mg m⁻³) in the northeast Aegean are probably due to the fact that in these relatively shallow coastal waters chl-a cannot readily be distinguished from particulate matter and/or yellow substances (dissolved organic matter), and so global chlorophyll algorithms (such as OC4-v4) are less reliable and seem to overestimate chl-a levels. However, the MODIS spatial distribution pattern of chl-a reflects the known north-south trophic gradient of the Aegean (e.g. Siokou-Frangou et al., 2002 and references therein). According to the chl-a composite, the phytoplanktonic biomass showed the highest values in the northeast Aegean (Fig. 8) coinciding unexpectedly with the highest fCO₂ values. In the rest

Fig. 7. Diagrams showing the relationship between (a) fCO₂ and sea surface temperature, (b) fCO₂ and sea surface temperature, (c) fCO₂ and salinity, (d) sea surface temperature and salinity and (e) fCO₂ and wind speed.
of the Aegean, chl-a remains at extremely low and almost uniform levels implying that the biological activity is not the driving force of the $fCO_{2}$ spatial variability. It is evident that in the northeast Aegean, the $fCO_{2}$ drawdown due to the photosynthetic activity cannot exceed the invasion of atmospheric CO$_2$ to the upper layer due to the surface cooling and the presence of less saline waters with relatively low pH.

Another process that directly affects the carbon dioxide concentrations is the production of calcitic and aragonitic plankton tests (i.e. $Ca^{2+}+2HCO_3^-\rightarrow CaCO_3+CO_2+H_2O$), which results in production of CO$_2$ and thus increases $fCO_{2}$. In the Aegean Sea, coccolithophores are often been reported as the dominant phytoplanktonic taxa during the cold period (Ignatiades et al., 2002). Additionally, Emiliania huxleyi var. huxleyi which dominates the winter coccolithophore assemblages exhibits an increase in the size of coccoliths and coccospheres, including a thicker inner tube cycle of the distal shield, during winter and early spring months, when the lowest sea surface temperatures occur together with higher $[HCO_3^-]$ concentrations (Triantaphyllou et al., 2009). However, during the winter period latitudinal differences of coccolithophore cell densities which could potentially explain the spatial variability of $fCO_{2}$ in the Aegean have not been observed (Ignatiades et al., 2002).

3.3. Air–sea CO$_2$ fluxes

The air–sea flux of CO$_2$ reflects the variability of both wind speed and the concentration difference of CO$_2$ across the air–water interface. The CO$_2$ flux densities were computed employing the above-mentioned different parameterisations of the gas transfer velocity and two wind data sources: (a) the onboard wind speed records (averaged into 20 min intervals) and (b) the monthly averaged model-generated wind speeds (MEAN dataset).

The model wind speeds have been produced with the aid of the POSEIDON weather forecasting system (Papadopoulos et al., 2002). The system is fully operational since 1999 and is based on the hydrostatic SKIRON model, which is a modified version of the ETA/NCEP model. It provides daily 72-h forecasts in two different model domains and resolutions: the first domain is extended over the entire Mediterranean Sea (~24 km), while the second higher resolution domain covers the Eastern Mediterranean (~10 km). For the need of this study, model outputs of the 24-h period from 6-h to 30-h forecasts (6 h spin-up time is considered) from each daily simulation of the 10-km model configuration were used. From the available hourly gridded wind data, the CRUISE and the MEAN datasets were constructed. The CRUISE dataset has been produced to evaluate the accuracy of the POSEIDON forecasts during the cruise, while the MEAN dataset to compute the mean monthly wind speed at the sampling time and position. Therefore, model winds were interpolated at each cruise track point based on the bilinear interpolation expression, $WS = \sum_{k=1}^{4}(w_k(WS_k))\sum_{k=1}^{4}w_k$, where, the $WS_k$ are the wind speed values at the four neighbouring model grid points at the particular time of sampling (for the CRUISE dataset) and at the same time averaging the wind speeds throughout February 2006 (for the MEAN dataset), while the weighting factor $w_k$ is taken as the reverse squared distance of each grid point from the sampling location.

Fig. 8. Spatial distribution of chlorophyll-a based on weekly averaged MODIS (4 km resolution) data for the time period of the cruise.

Fig. 9. Comparison of the in situ recorded wind speeds with the model predicted (cruise) and the monthly averaged model-derived (mean) wind speeds. The in situ and the mean monthly model winds were used to calculate the air–sea CO$_2$ fluxes.
Time series of the in situ recorded and the model-generated wind speeds are presented in Fig. 9. The average of the onboard measured and model wind speeds are 9.8 and 8.8 m s\(^{-1}\), while their standard deviations are 2.8 and 2.5 m s\(^{-1}\), respectively. The high overall correlation (0.70) in combination with the relatively low Root Mean Square Error (RMSE: ~2.28) and the low mean observed-to-model bias (~0.99) reveal a good agreement between in situ recorded and model-generated wind speeds.

Even though the data of the onboard meteorological station are the most appropriate to calculate the gas transfer coefficient, the previously described comparison revealed that the application of the CRUISE dataset obtained by the POSEIDON model provides similar results. However, the MEAN dataset that corresponds to the monthly mean model-derived wind speed during February 2006 (Fig. 9) implies that throughout the month the wind regime was smoother and the in situ dataset obtained by the POSEIDON model provides previously described comparison revealed that the application of the most appropriate to calculate the gas transfer coefficient, the speed sources.

The results of the four formulations obtained with both wind speed sources (in situ recorded and MEAN dataset) in all three regions of the Aegean show that during February 2006 the net flux of CO\(_2\) through the air–sea interface is negative (Table 1; Fig. 10). For the northeastern Aegean Sea the results obtained using the onboard wind speed records are a factor of 66–84% higher than the results obtained with the second approach (Table 1). This significant disparity is mainly due to the difference between the wind speeds recorded onboard and the monthly averaged wind speed given by the POSEIDON model for each specific A\(\text{CO}_2\) observation and probably reflects the high wind speeds during the cruise. The average instantaneous wind speeds recorded in this area was 11.4±1.6 m s\(^{-1}\) when the average of the monthly mean model-derived wind speed was 6.0±0.8 m s\(^{-1}\). The fluxes obtained with the onboard wind speeds range from ~7.8 to ~16.0 mmol m\(^{-2}\) d\(^{-1}\) using LM86 and MG01 relationships, respectively. This large difference is due to the different formulations of the LM86 and MG01 relationships between gas exchange and wind speed. The LM86 can be closely approximated by a quadratic relationship over a wind speed range of 0–15 m s\(^{-1}\), whereas the MG01 relationship is a cubic relationship between the wind speed and the gas transfer velocity. For both relationships, the gas transfer increases at an exponential rate as a function of the wind speed, which explains the large difference in the calculations. On the other hand, for the second approach the value of ~3.7 mmol m\(^{-2}\) d\(^{-1}\) found with the MG01 is in the same range of values of CO\(_2\) through the air–sea interface.

Table 1
Air–sea CO\(_2\) fluxes in the Aegean Sea during February 2006 calculated using the two different approaches (a) the instantaneous wind speed recorded on board (in situ) and (b) the monthly averaged model-derived wind (MEAN) and different gas transfer coefficients.

<table>
<thead>
<tr>
<th>(\Delta F/\text{CO}_2) ((\mu\text{atm}))</th>
<th>Wind speed (m s(^{-1}))</th>
<th>Air–sea CO(<em>2) fluxes ((F</em>{\text{CO}_2}), mmol m(^{-2}) d(^{-1})) calculated using different gas transfer coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in situ MEAN</td>
<td>in situ MEAN</td>
</tr>
<tr>
<td>North of 39°45’N</td>
<td>11.4±1.6 6.0±0.8</td>
<td>7.8±2.2 2.7±1.1</td>
</tr>
<tr>
<td>36°45’N–39°30’N</td>
<td>9.9±3.0 7.3±1.0</td>
<td>6.6±2.9 3.9±1.3</td>
</tr>
<tr>
<td>South of 36°45’N</td>
<td>8.6±1.8 6.0±0.4</td>
<td>5.1±1.9 2.6±0.5</td>
</tr>
<tr>
<td>Aegean Sea</td>
<td>9.8±2.8 6.8±1.0</td>
<td>6.2±2.7 3.5±1.2</td>
</tr>
</tbody>
</table>

Fig. 10. Air–sea CO\(_2\) fluxes in the Aegean Sea during February 2006 calculated using different gas transfer coefficients and the different wind sources (a) the in situ recorded wind speed and (b) the monthly averaged model-derived wind (MEAN).
Table 2

<table>
<thead>
<tr>
<th>Region</th>
<th>Mean CO₂ Flux (mmol m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW Mediterranean Sea—WMC99⁴</td>
<td>−3.8</td>
</tr>
<tr>
<td>Gulf of Cadiz—W92⁴</td>
<td>−19.5</td>
</tr>
<tr>
<td>Ria de Vigo—LMB6⁵</td>
<td>−1.53 to −0.05</td>
</tr>
<tr>
<td>Outer US Middle Atlantic Bight—LM86⁶</td>
<td>−1.4</td>
</tr>
<tr>
<td>Outer US Middle Atlantic Bight—W92⁴</td>
<td>−2.5</td>
</tr>
<tr>
<td>East China Sea—LMB6⁶</td>
<td>−6.4</td>
</tr>
</tbody>
</table>

⁴ Copin-Montégut and Bégo (2002).
⁵ Gonzalez-Davila et al. (2003).
⁶ Gago et al. (2003).
⁷ DeGrandpre et al. (2002).
⁸ Wang et al. (2000).

obtained with the other gas transfer coefficients (Table 1; Fig. 10). The wind speeds of the MEAN dataset are in a range of values where the different formulations give similar results for the gas transfer velocity.

For the other two sub-regions of the Aegean, between 39°30’N and 36°45’N and south of 36°45’N, the fluxes calculated from the shipboard winds were 40–68% higher than those obtained from the MEAN dataset (Table 1; Fig. 10). In the area south of 36°45’N, despite the slightly higher ΔCO₂, the attained CO₂ flux densities using both wind sources were lower in comparison to the area between 39°30’N and 36°45’N, probably related to the occurrence of lower wind speeds.

The results from the different gas transfer formulations show that the Aegean Sea as a whole absorbs CO₂ at a rate ranging from −6.2 (LM86) to −11.8 (MG01) mmol m⁻² d⁻¹ with the in situ recorded wind and at almost half rate (−3.5 (LM86) and −5.5 (W92)) mmol m⁻² d⁻¹ with the monthly mean model-derived wind speed (Table 1). The obtained results are in agreement with the direction of the CO₂ fluxes reported in other temperate continental shelf seas. Existing data on air–sea CO₂ fluxes suggest that temperate marginal seas act as sinks for atmospheric CO₂ (e.g. East China Sea, Tsunogai et al. 1999; Gulf of Biscay, Frankignoulle and 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 air–sea CO₂ fluxes obtained in the Aegean Sea during February 2006 to the data from other coastal seas during winter period (Table 2), our study shows that when the shipboard wind speeds are used the Aegean Sea acts as a rather strong sink for the atmospheric CO₂. Since wind speed modulates the intensity of the flux, the smoother monthly mean model-derived wind speeds underestimate the CO₂ uptake rates and the Aegean Sea appears as a moderate sink for CO₂. The significant differences in the estimation of air–sea CO₂ fluxes between the two approaches imply that the shipboard wind speeds should be used for in situ investigations when the recorded wind speeds are typical of the meteorological conditions usually encountered in the study area. For budgeting approaches, the fluxes depend too much on the local and in situ weather situation and therefore, it appears to be more reasonable to use long-term or high-resolution wind field data rather than in situ or short-term winds. For the Aegean Sea where systematic measurements are missing and the satellite wind data are considered inadequate, mainly due to the complicated land/sea distribution of the region and the coarse spatial resolution of satellite retrievals that cannot capture local circulations, the utilisation of a high-resolution model can be considered as an alternative useful tool for estimating the weather conditions prevailing in the area.

3.4. Mixed layer depth and air–sea exchange

If it is assumed that within the mixed layer the carbon dioxide concentration is homogeneous, no internal processes that affect the gas content take place and the conditions at the air–sea interface remain constant, one can estimate the time required to achieve equilibrium with the atmosphere. The mixed layer depth (MLD) in the three different sub-regions of the Aegean sea was calculated from each single profile of the 46 CTD casts performed during the cruise (Sofianos and Theocharis, unpublished data), using a ΔCO₂ = 0.05 criterion (Hopkins et al., 1992). The average mixed layer depth was (a) north of 39°45’N 11 ± 10 m, (b) between 39°30’N and 36°45’N 168 ± 100 m and (c) south of 36°45’N 109 ± 39 m. Using both wind regimes and the four different transfer velocity equations it was estimated that at the northeastern Aegean the equilibration time is less than 3 days using the in situ measured winds and less than 10 days using the monthly averaged POSEIDON wind speed. In the central part of the Aegean, it would take about 1–2.5 months to equilibrate its CO₂ content with the atmosphere depending on the gas transfer formulation used; the time being higher (80 days) using the wind speeds of the MEAN dataset. At the Cretan sea, the air–sea exchange will be completed within 1–1.5 months using the shipboard recorded winds, while it will take 1.5–3 months using the model-derived wind speeds. The shallow mixed layer depth in the area north of 39°45’N suggests that during February 2006 the buoyancy input through the Dardanelles and the rivers induces increase of stratification. The surface layer of the North Aegean is an effective isolator between the deep layers of the North Aegean and the atmosphere, absorbing large amounts of heat and buoyancy, hindering dense water formation (Zervakis et al., 2000) and thus resulting in the short equilibration time of CO₂ with the atmosphere during February 2006. Southwards of 39°30’N, within the mixed layer the −13% mean CO₂ under-saturation amounts to a mean deficiency of about 300 mmol CO₂ in the central Aegean (MLD = 168 m) and about 190 mmol CO₂ in the Cretan Sea (MLD = 109 m). The initial CO₂ uptake rate (Table 1) is less than 22% (MG01-in situ winds) of the deficiency per day. The CO₂ influx rate will of course decrease as the concentration gradient decreases and the required time to restore the gaseous equilibrium with the atmosphere increases. Furthermore, the ‘real’ equilibration time of CO₂ is much longer because CO₂ is a small part of the dissolved inorganic carbon which buffers changes in CO₂ concentration and thereby slows down the equilibration (Zeebe and Wolf-Gladrow, 2001).

During winter, the high observed transfer of carbon dioxide due to the increased wind force is additionally provoked by the temperature decrease of surface waters that drives a decrease in fCO₂ values and enhances the penetration of the atmospheric CO₂. The extended shelves of the Aegean (Samothraki Plateau, Thermanlous Gulf, Lesvos shelf, Cyclades Plateau) are ideal sites of dense water formation due to the limited volume of water exchanging buoyancy with the atmosphere (Zervakis et al., 2005). The dense water formed due to the water cooling in the shallow shelves of the Aegean and the subsequent slow spreading and mixing transports the water enriched in dissolved gases into the deeper layers of the Aegean. 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 CO₂ in the East China Sea during winter.

Although more investigations, including intensive spatial and temporal high-resolution observations, are required to elucidate the role of the Aegean in the process of transfer of atmospheric CO₂ into the deep horizons of the Eastern Mediterranean, this
study reports that, at least during winter the Aegean Sea acts as a CO$_2$ sink, thereby possibly contributing to the enhancement of CO$_2$ storage in the open ocean.

4. Conclusions

This study presents the first ‘winter-time’ snapshot of the JCO$_2$ distribution in the surface waters of the Aegean Sea. The analysed data indicate that the area is under-saturated with respect to the overlying marine air causing a net CO$_2$ uptake from the atmosphere. In the colder and shallower shelves of the northeast Aegean, the recorded higher JCO$_2$ could be transported into the deeper layers of the Aegean by the dense waters formed in the area, although such events do not take place frequently, due to the insulating effect of the surface BSW layer and river outflow. Southwards of 39°30′N, the strong vertical convection results in a deep mixed layer that in combination with the observed CO$_2$ under-saturation leads to a long influx period until equilibrium with the atmosphere is achieved. At the moment it is premature to conclude on the behaviour of the Aegean. However, if the dense water formation process is active, it is possible that during winter the Aegean could act as a ‘continental shelf pump’ that absorbs atmospheric CO$_2$.

Extensive continuous shipboard measurements of JCO$_{mm}$ and JCO$_{0}$ during all seasons would be necessary to establish carbon budgets, annual air–sea CO$_2$ exchanges and safely quantify the role of the Aegean Sea in the context of the marginal seas 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.

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