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Partial pressure and air–sea CO_2 flux in the Aegean Sea during February 2006

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ABSTRACT

Data on the distribution of fCO_2 were obtained during a cruise in the Aegean Sea during February 2006. The fCO_2 of surface water (fCO_2^{sw}) was lower than the atmospheric fCO_2 (fCO_2^{atm}) throughout the area surveyed and ΔfCO_2 values varied from −34 to −61 μatm. The observed under-saturation suggests that surface waters in the Aegean represent a sink for atmospheric CO_2 during the winter of 2006. Higher fCO_2^{sw} values were recorded in the 'less warm' and 'less saline' shallow northernmost part of the Aegean Sea implying that the lower seawater temperature and salinity in this area play a crucial role in the spatial distribution of fCO_2^{sw}.

A first estimate of the magnitude of the air–sea CO_2 exchange and the potential role of the Aegean Sea in the transfer of atmospheric CO_2 was also obtained. The air–sea CO_2 fluxes calculated using different gas transfer formulations showed that during February 2006, the Aegean Sea absorbs atmospheric CO_2 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 CO_2.

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 CO_2 into the deep horizons of the Eastern Mediterranean.

1. Introduction

The number of measurements of the partial pressure of CO_2 (pCO_2) 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 CO_2 fluxes of the global ocean margin due primarily to the lack of pCO_2 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 CO_2 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 km^2 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 CO_2, 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 (Aït-Ameur and Goyet, 2006). Recently, Krasakopoulou et al. (2007) reported that the Thermaikos Gulf (Eastern Mediterranean-NW Aegean Sea) acts as weak sink of atmospheric CO_2, based on calculated fCO_2 values from dissolved inorganic carbon and total alkalinity data collected during May 1997.

Basin-scale estimates of the CO_2 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 CO_2, with a climatological integrated flux of $0.35{-}1.85 \times 10^{12}$ mol y^{-1}. A large uncertainty, however, is attached to the magnitude and direction of this flux. Based on time series of

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fCO_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 $-0.15\,\mathrm{mol\ CO_2\,m^{-2}\,y^{-1}}$, using the Liss and Merlivat (1986) or Wanninkhof (1992) gas transfer formulation, respectively. Extrapolating this rate over the surface area of the Mediterranean Sea ($2.5\times10^{12}\,\mathrm{m^2}$) yielded a flux between -2.5×10^{11} and $-3.8\times10^{11}\,\mathrm{mol\ CO_2\,y^{-1}}$. 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 pCO_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 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 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 xCO_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 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 ($S>38.8$ psu) and warm (16–25 °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 ($S\sim30$ psu) and cold (9–22 °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

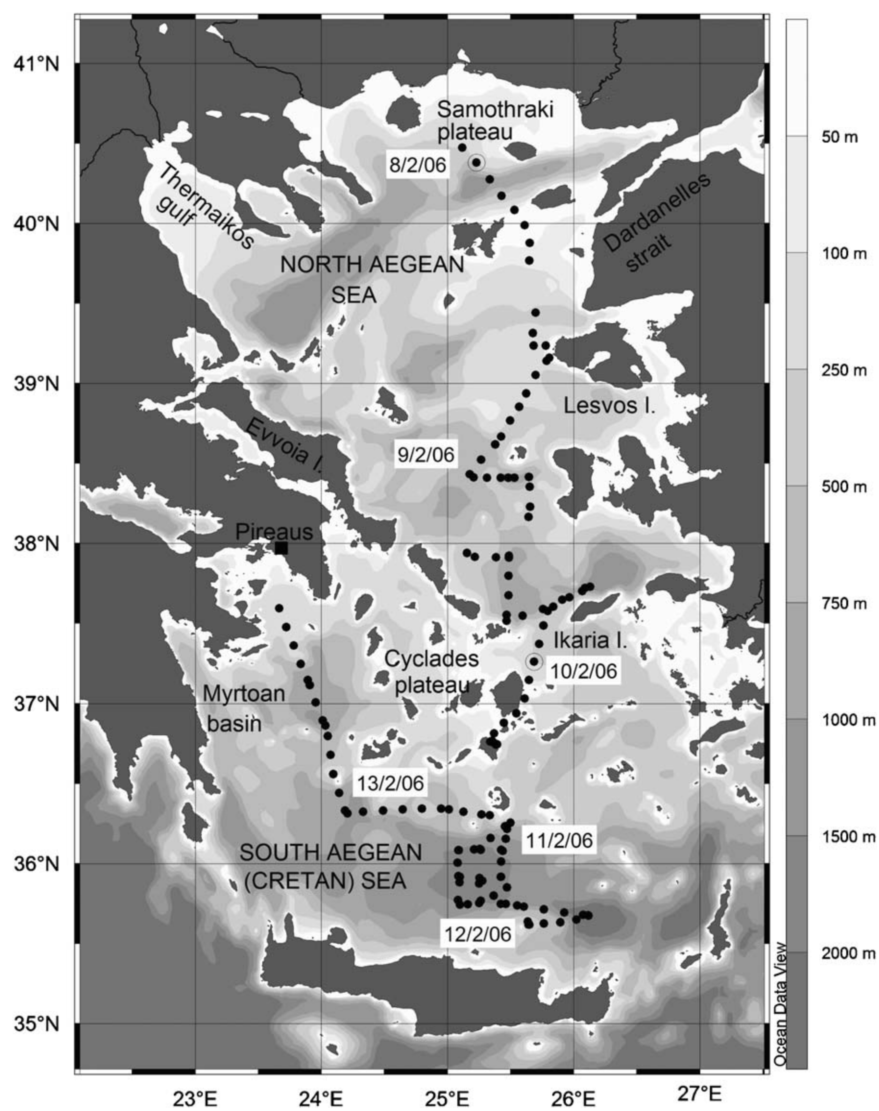

Fig. 1. Bathymetric map of the study area showing the geographic locations referred in the manuscript. The dots indicate the ship's track and the dates show the evolution of the cruise.

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 CO_2 were performed in the Aegean Sea during February 2006 (8–13/2/2006) onboard the *R/V Aegaeo*. 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 CO_2 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 CO_2 standards of 257 and 345 ppmV CO_2 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 CO_2 concentrations were more than accurate. The accuracy of the entire system was better than 0.5 ppmV for xCO_2^{atm} and 1.0 ppmV for xCO_2^{sw}.

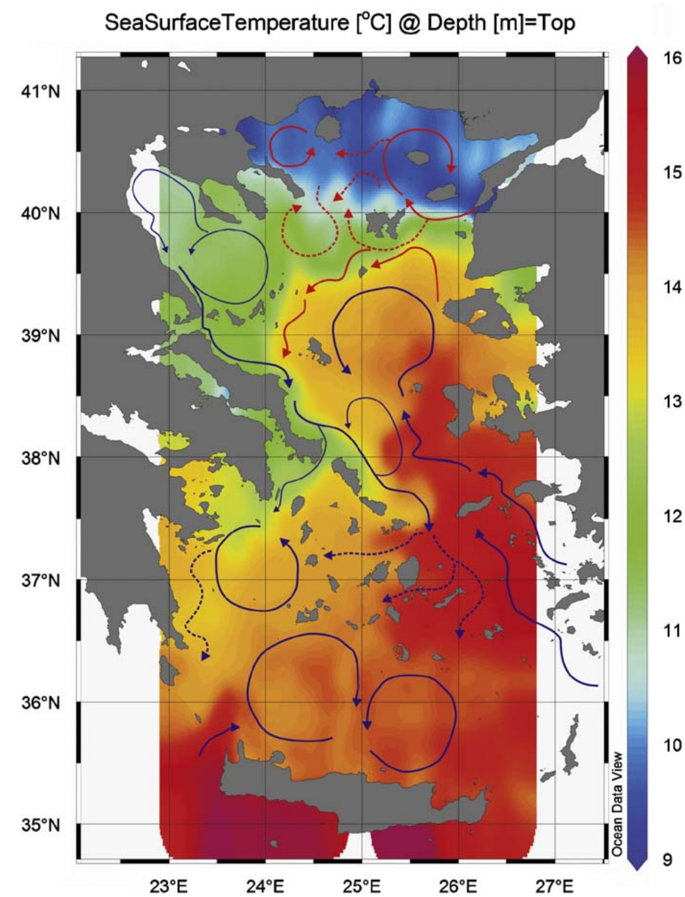

Fig. 2. Spatial distribution of sea surface temperature (weekly averaged MODIS data-4 km resolution) for the time period of the cruise. Superimposed is the surface circulation of the Aegean (solid lines represent permanent features and dashed lines recurrent or transient features) (adapted from Zervakis et al., 2005).

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 xCO_2 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 CO_2 in dry air (xCO_2) which then is converted into CO_2 fugacity (fCO_2). Since CO_2 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 fCO_2^{atm} is calculated according to:

$$fCO_2{}^{atm} = xCO_2{}^{atm}(P - pH_2O)\exp[(B_{11} + 2\delta_{12})P/RT]$$

where pH_2O 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 CO_2, δ_{12} is the correction for an air-CO_2 mixture (Weiss, 1974), R is the gas constant and T is the absolute temperature. The calculation of the fugacity in surface seawater (fCO_2^{sw}) includes the empirical temperature correction for fCO_2 proposed by Takahashi et al. (1993) (i.e. $(\partial fCO_2/\partial T)/fCO_2 = 0.0423\,°C^{-1}$) 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 fCO_2 values of about 2%. The fugacity in seawater is calculated according to:

$$fCO_2{}^{sw} = xCO_2{}^{sw}(P - pH_2O_{eq})\exp[(B_{11} + 2\delta_{12})P/RT] \times \exp[(T_{sw} - T_{eq})0.0423]$$

2.4. Calculation of the air–sea CO_2 fluxes

The CO_2 flux (F_{CO_2}, mmol m^{-2} d^{-1}) across the air–sea interface can be computed from the sea-air gradient of fCO_2 ($\Delta fCO_2 = fCO_2^{sw} - fCO_2^{atm}$, μatm), the solubility coefficient K_o of 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: $F_{CO_2} = K_o \times k \times \Delta fCO_2$. The difference between fCO_2^{sw} and fCO_2^{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 (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 $k = 0.3u_{10}^2(S_c/660)^{-0.5}$, where S_c is the Schmidt number of CO_2 in seawater, 660 is the S_c for 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, $k_{660} = 0.028u_{10}^3$, or $k = 0.228u_{10}^2 (S_c/660)^{-0.5}$, which, compared with previous calculations using the W92 parameterisation, resulted in a significant increase in the calculated oceanic global annual 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 CO_2 to determine k and showed that k can be described as $k_{660} = 3.3 + 0.026u_{10}^3$, where k_{660} is the k normalised to S_c of 660 in cm h^{-1} (which equals the S_c for 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 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 WMG99 and MG01, respectively, were applied to determine the CO_2 flux across the sea-air interface using cruise data. LM86, W92 and MG01 normalise their parameterisations with respect to the S_c of CO_2 in seawater at 20 °C. Also, we note here that while LM86 note 600 as the S_c of CO_2 at 20 °C, W92 and MG01 note 660 as the S_c of CO_2 at 20 °C. However, k being a function of either $(S_c/600)^{-0.5}$ or $(S_c/660)^{-0.5}$, 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,

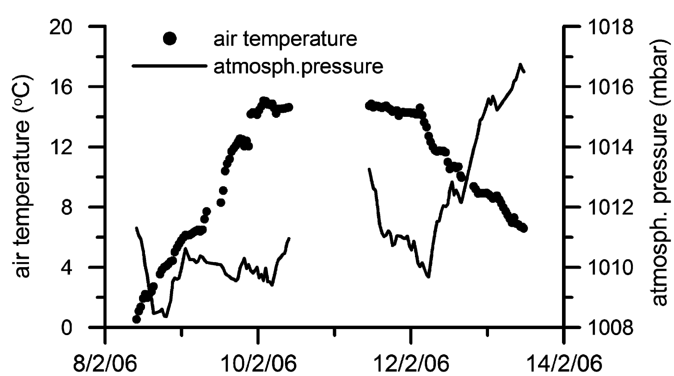

Fig. 3. Time evolution of air temperature and atmospheric pressure in the Aegean Sea in the period between 8 and 13 February 2006.

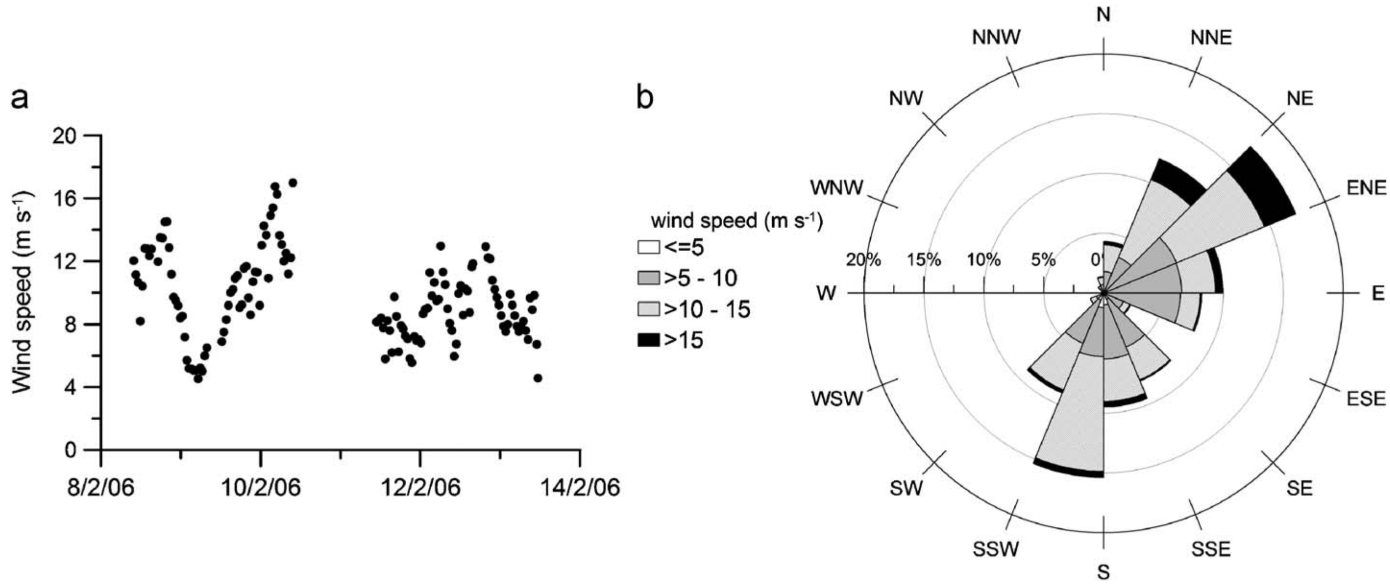

Fig. 4. (a) Time evolution of the onboard recorded wind speed and (b) wind rose showing the predominant wind direction in the sampling area during 8–13 February 2006.

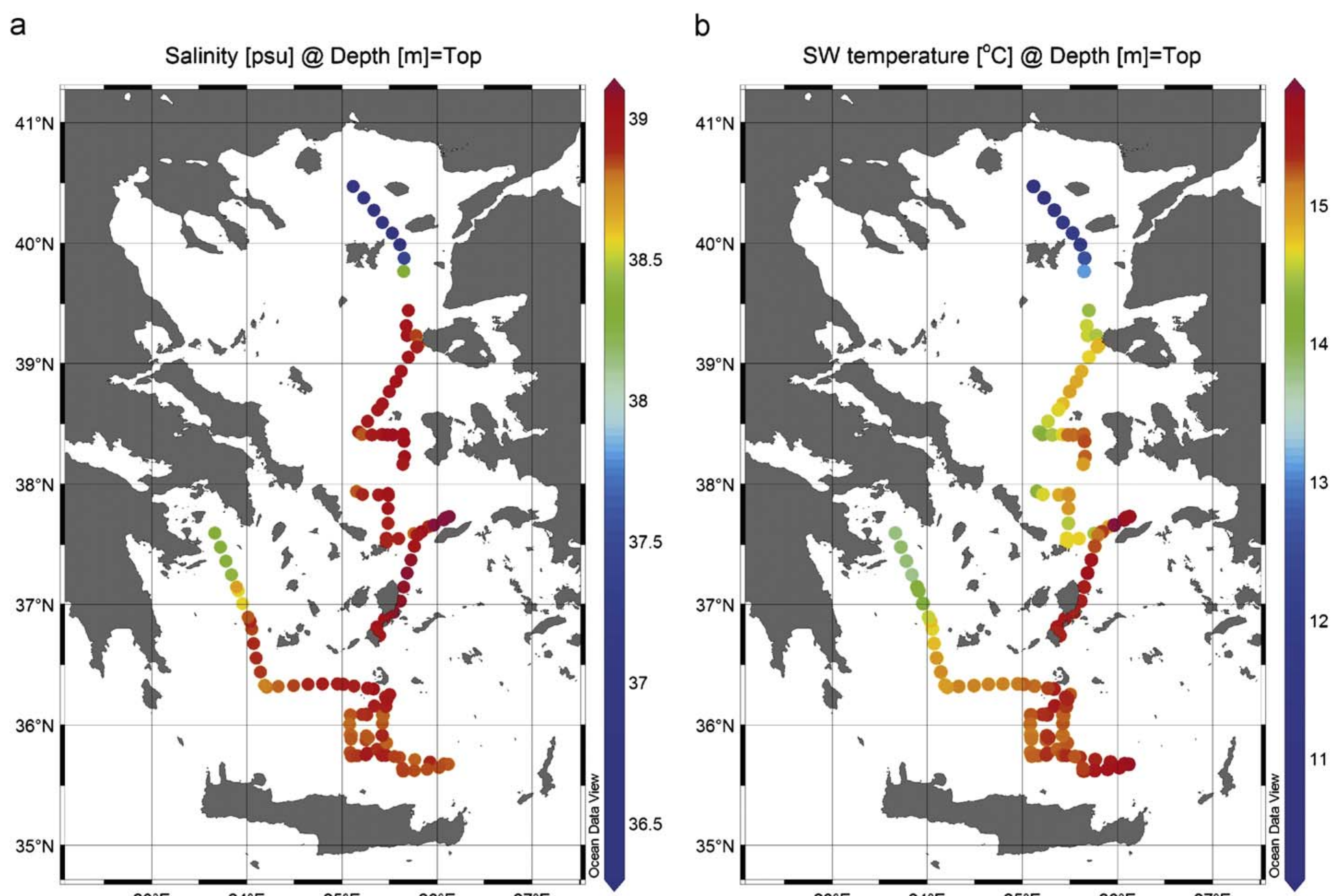

Fig. 5. Spatial distribution of (a) salinity and (b) sea surface temperature in the Aegean Sea during 8–13 February 2006.

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 fCO_2 and relationships with seawater properties

The xCO_2 data recorded during the cruise allow us to plot the first map of fCO_2^{sw} for the Aegean Sea in winter (Fig. 6). The average surface water fCO_2 was $323 \pm 5\,\mu$atm and ranged between 312 and 338 µatm. By comparison, atmospheric fCO_2 ranged between 361 and 380 µatm having an average value of $369 \pm 4\,\mu$atm. The fCO_2 of surface water of the entire survey area was lower than the atmospheric fCO_2 suggesting thus under-saturation of surface waters with respect to the overlying atmosphere. This under-saturation leads to ΔfCO_2 values from -34 to more than $-60\,\mu$atm, and hence surface waters in the Aegean represent a sink for atmospheric CO_2 during winter 2006. The saturation state of the surface waters expressed by the saturation ratio, SR ($SR = (C^{sw}/C^{atm}) \times 100$, where C^{sw} and C^{atm} 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 fCO_2^{sw} 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 fCO_2^{sw} values ranging between 328 and 338 µatm (average ± std. dev.: $331 \pm 4\,\mu$atm), (b) between 39°30′N and 36°45′N that comprises the central Aegean, Cyclades Plateau and Myrtoan Sea, characterised by lower fCO_2^{sw} values (average ± std. dev.: $323 \pm 4\,\mu$atm) and (c) south of 36°45′N namely the Cretan Sea, with somewhat lower fCO_2^{sw} levels (average ± std. dev.: $320 \pm 5\,\mu$atm).

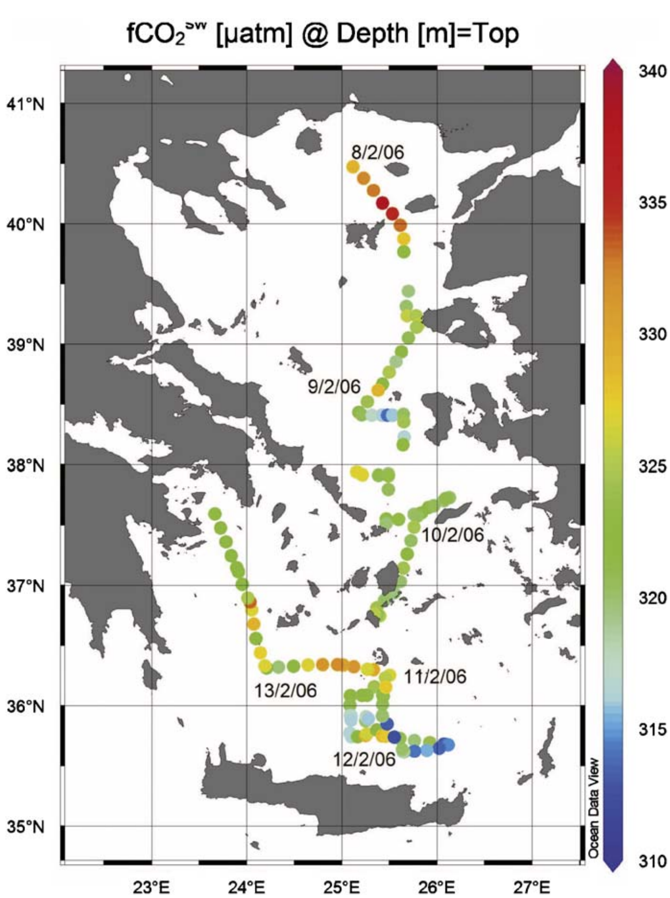

Fig. 6. Spatial distribution of fCO_2^{sw} (µatm) in the surface waters of the Aegean Sea during 8–13 February 2006.

The fCO_2 of surface seawater is controlled by the following processes: thermodynamical change, air–sea exchange, biological activity and mixing processes. The temperature effect on fCO_2^{sw} is opposite in direction to the biological production; temperature increases lead to higher fCO_2^{sw}, whereas photosynthetic activity leads to drawdown of CO_2 and thus fCO_2^{sw} decreases. Generally, a great part of the fCO_2^{sw} variations are due to the temperature dependence of the carbonate equilibria. These functional variations of fCO_2^{sw} with temperature may obscure the correlation with the other variables. In order to eliminate the thermodynamic effect on fCO_2, the fCO_2 data are normalised to a fixed temperature of 14.9 °C ($NfCO_2^{sw}$), 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 fCO_2 would reflect primarily the influence of the invasion and evasion of atmospheric CO_2, biological uptake or production of CO_2 and mixing with other water masses.

Fig. 7 shows the correlations of the temperature normalised fCO_2^{sw} ($NfCO_2^{sw}$) with other measured variables (surface seawater temperature, salinity, wind speed), as well as the fCO_2^{sw}-temperature relationship and the $T-S$ diagram.

The $NfCO_2^{sw}$ 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 $NfCO_2^{sw}$ 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 fCO_2 and cold waters of higher fCO_2. The invasion of atmospheric CO_2 into the upper layer of the northeast Aegean as a result of surface cooling is the process that probably contributes to the observed higher fCO_2^{sw} 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 CO_2 under-saturation which then results in an intensified uptake of atmospheric CO_2 on the continental shelf. The presence of low salinity waters could also contribute to the occurrence of the elevated fCO_2^{sw} values in the northeast Aegean. Although any other parameter of the CO_2-carbonate system was not measured on this cruise, pH and fCO_2^{sw} 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 fCO_2^{sw} values (Triantaphyllou et al., 2009).

Fig. 7c shows the dependency of the temperature normalised fCO_2^{sw} data on salinity and reveals that surface waters having almost the same salinity may be characterised by different $NfCO_2^{sw}$ values. It is interesting to note that although the temperature effect was removed, the signal of the different waters remains on the $NfCO_2^{sw}$. Hence the $NfCO_2^{sw}$ 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 $NfCO_2^{sw}$ 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 $NfCO_2^{sw}$ levels. It is assumed that high wind speeds or rapid wind speed changes did not cause rapid changes in surface water fCO_2^{sw}, as a result of the strong buffering of ocean CO_2 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

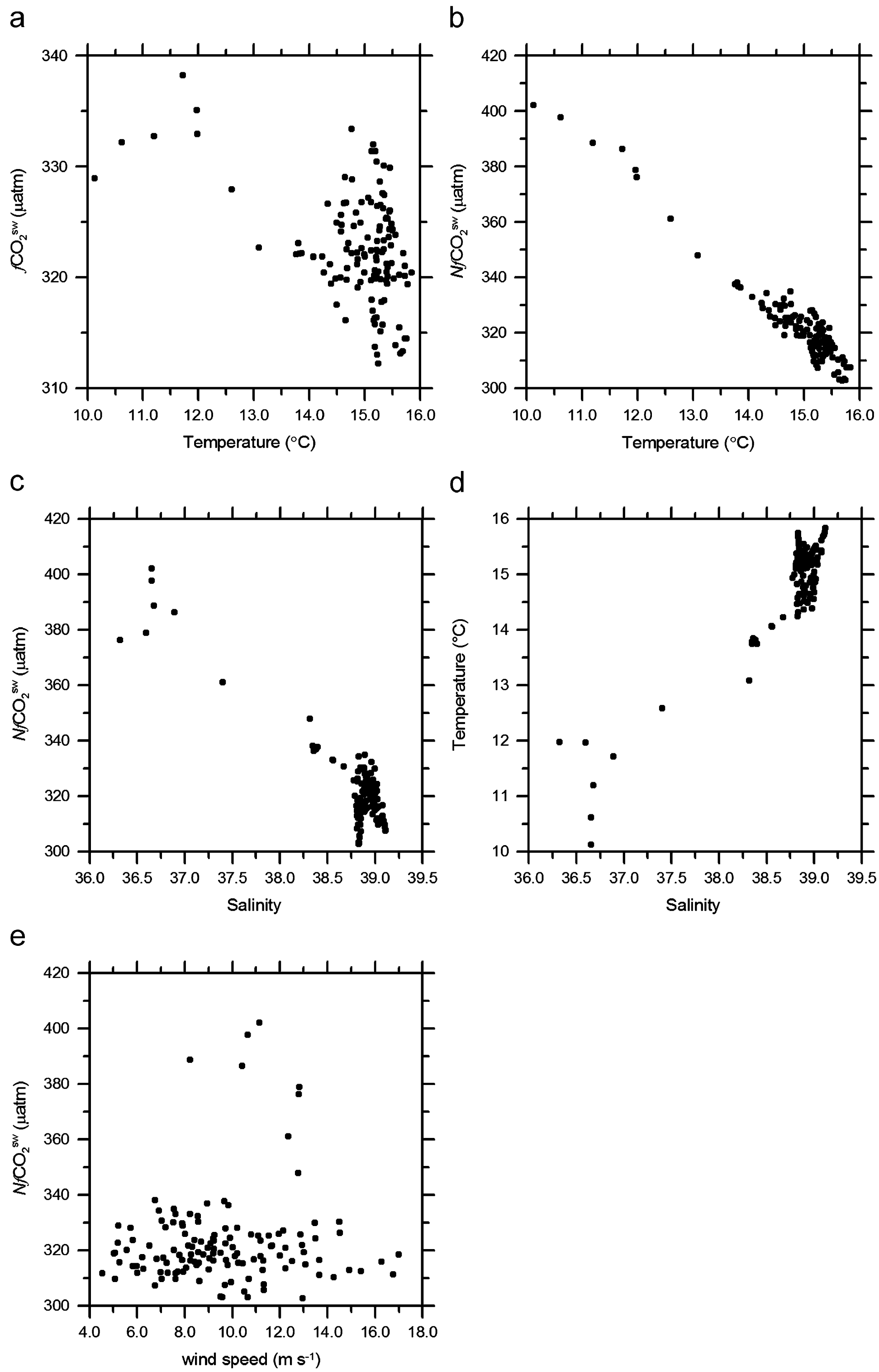

Fig. 7. Diagrams showing the relationship between (a) fCO_2 and sea surface temperature, (b) $NfCO_2^{sw}$ and sea surface temperature, (c) $NfCO_2^{sw}$ and salinity, (d) sea surface temperature and salinity and (e) $NfCO_2^{sw}$ and wind speed.

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 fCO_2^{sw} values. In the rest 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^{sw} spatial variability. It is evident that in the northeast Aegean, the fCO_2^{sw} 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. $Ca^{2+}+2HCO_3^- \Leftrightarrow CaCO_3+CO_2+H_2O$), which results in production of CO_2 and thus increases fCO_2^{sw}. 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^{sw} in the Aegean have not been observed (Ignatiades et al., 2002).

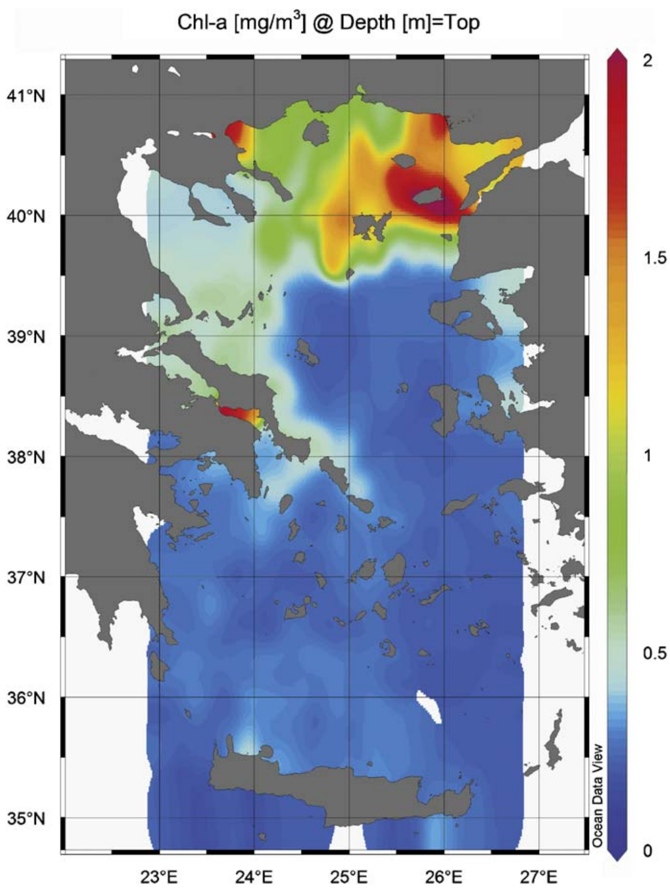

Fig. 8. Spatial distribution of chlorophyll-*a* based on weekly averaged MODIS (4 km resolution) data for the time period of the cruise.

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.

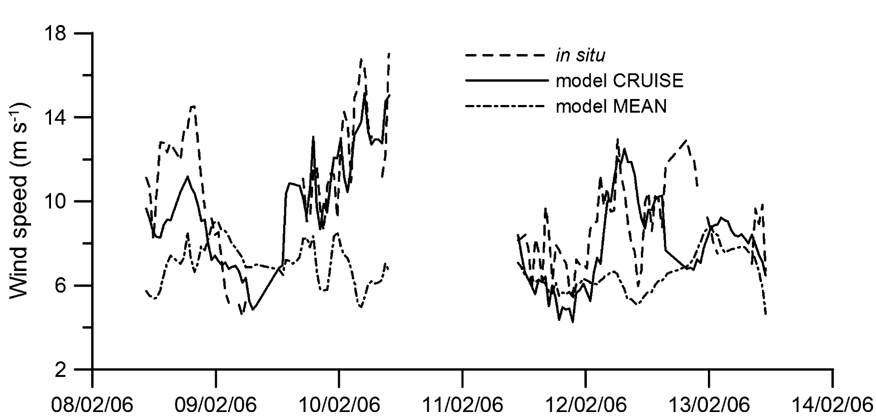

Fig. 9. Comparison of the *in situ* recorded wind speeds with the model predicted (cruise) and the monthly averaged model-derived (mean) wind speeds. The *in situ* and the mean monthly model winds were used to calculate the air–sea CO_2 fluxes.

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* recorded as well as the model-derived wind speeds during 8–13 February could be considered as extreme and not typical events of the meteorological conditions prevailing in the study area. Choosing a representative and complete wind speed dataset is a major step toward reducing uncertainty in flux calculations. The use of the wind data that correspond to the particular sampling time could lead to an unrealistic evaluation of the carbon dioxide fluxes (Bozec et al., 2005; Wang et al., 2005; Shim et al., 2007). For comparison, in addition to the shipboard wind speeds, the model-derived MEAN dataset that represents the mean monthly wind speed at the sampling time and position will be applied. The use of time averaged winds can lead to biases of the air–sea CO_2 fluxes. Bates and Merlivat (2001) showed, using data from a site near Bermuda, that the air–sea CO_2 flux is up to three times greater if hourly wind data are used rather than daily averaged values. Similar work, using model results on a global scale rather than localised data, by Chapman et al. (2002) for dimethylsulfide fluxes showed that the gas emission fluxes were often 10–60% higher when using 20-min rather than monthly averaged wind speeds. These errors arise because in the non-linear gas transfer relationships, periods of sharp-gradient wind speeds contribute disproportionately to the time integrated flux, while if the high frequency wind speed data are averaged this effect is lost.

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 ΔfCO_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

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.

	ΔfCO_2 (μatm)	Wind speed (m s^{-1})		Air–sea CO_2 fluxes (F_{CO_2}, mmol m^{-2} d^{-1}) calculated using different gas transfer coefficients							
				LM86		W92		WM99		MG01	
		in situ	MEAN	*in situ*	MEAN	*in situ*	MEAN	*in situ*	MEAN	*in situ*	MEAN
North of 39°45′N	44±7	11.4±1.6	6.0±0.8	−7.8±2.2	−2.7±1.1	−14.7±4.9	−4.2±1.7	−15.8±6.7	−2.5±1.3	−16.0±6.3	−3.7±1.4
36°45′N–39°30′N	46±7	9.9±3.0	7.3±1.0	−6.6±2.9	−3.9±1.3	−12.3±7.0	−6.2±2.0	−13.1±11.0	−4.3±1.9	−13.4±10.0	−5.3±1.8
South of 36°45′N	47±5	8.6±1.8	6.0±0.4	−5.1±1.9	−2.6±0.5	−8.6±3.7	−4.2±0.7	−7.2±4.7	−2.3±0.5	−8.0±4.3	−3.5±0.5
Aegean Sea	47±5	9.8±2.8	6.8±1.0	−6.2±2.7	−3.5±1.2	−11.2±6.3	−5.5±1.9	−11.3±9.6	−3.6±1.7	−11.8±8.8	−4.7±1.7

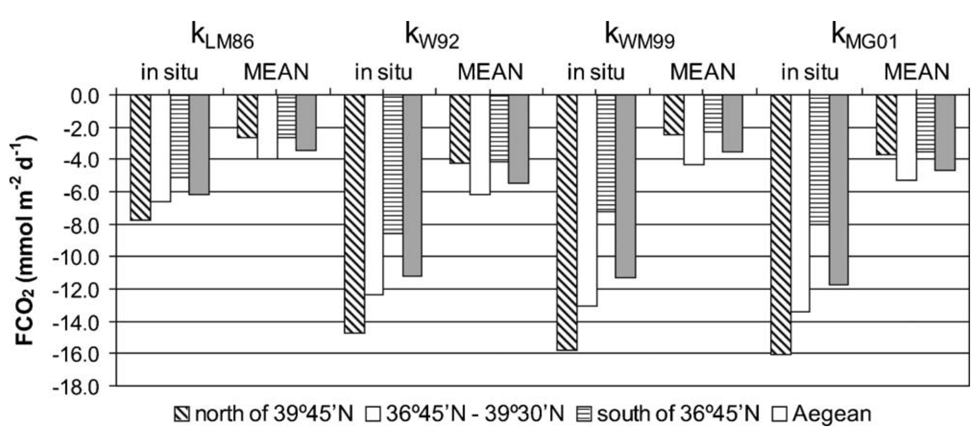

Fig. 10. Air–sea CO_2 fluxes in the Aegean Sea during February 2006 calculated using different gas transfer coefficients and the different wind sources (a) the *in situ* recorded wind speed and (b) the monthly averaged model-derived wind (MEAN).

Table 2
Representative air–sea CO_2 fluxes from mid-latitude continental seas during winter.

Wintertime F_{CO_2} ($mmol\,m^{-2}\,d^{-1}$) in other continental seas	
NW Mediterranean Sea—WMG99[a]	−3.8
Gulf of Cadiz—W92[b]	−19.5
Ria de Vigo—LM86[c]	−1.53 to −0.05
Outer US Middle Atlantic Bight—LM86[d]	−1.4
Outer US Middle Atlantic Bight—W92[d]	−2.5
East China Sea—LM86[e]	−6.4

[a] Copin-Montégut and Bégovic (2002).
[b] Gonzalez-Davila et al. (2003).
[c] Gago et al. (2003).
[d] DeGrandpre et al. (2002).
[e] 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 ΔfCO_2, the attained CO_2 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 adsorbs CO_2 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 CO_2 fluxes reported in other temperate continental shelf seas. 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 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 CO_2 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 CO_2. Since wind speed modulates the intensity of the flux, the smoother monthly mean model-derived wind speeds underestimate the CO_2 uptake rates and the Aegean Sea appears as a moderate sink for CO_2. The significant differences in the estimation of air–sea CO_2 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 $\Delta\sigma_\theta = 0.05$ 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 CO_2 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 CO_2 with the atmosphere during February 2006. Southwards of 39°30′N, within the mixed layer the ~13% mean CO_2 under-saturation amounts to a mean deficiency of about 300 mmol CO_2 in the central Aegean (MLD = 168 m) and about 190 mmol CO_2 in the Cretan Sea (MLD = 109 m). The initial CO_2 uptake rate (Table 1) is less than 22% (MG01-*in situ* winds) of the deficiency per day. The CO_2 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 CO_2 is much longer because CO_2 is a small part of the dissolved inorganic carbon which buffers changes in CO_2 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 fCO_2^{sw} values and enhances the penetration of the atmospheric CO_2. The extended shelves of the Aegean (Samothraki Plateau, Thermaikos 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 CO_2 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 CO_2 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 fCO_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 shallow shelves of the northeast Aegean, the recorded higher fCO_2^{sw} 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 insulation 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 fCO_2^{atm} and fCO_2^{sw} 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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