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CO_2 exchange in a temperate marginal sea of the Mediterranean Sea: processes and carbon budget

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Abstract

Marginal seas play a potentially important role in the global carbon cycle; however, due to differences in the scales of variability and dynamics, marginal seas are seldom fully accounted for in global models or estimates. Specific high-resolution studies may elucidate the role of marginal seas and assist in the compilation of a complete global budget. In this study, we investigated the air-sea exchange and the carbon cycle dynamics in a marginal sub-basin of the Mediterranean Sea (the Adriatic Sea) by adopting a coupled transport-biogeochemical model of intermediate complexity including carbonate dynamics. The Adriatic Sea is a highly productive area owed to riverine fertilisation and is a site of intense dense water formation both on the northern continental shelf and in the southern sub-basin. Therefore, the study area may be an important site of CO_2 sequestration in the Mediterranean Sea. The results of the model simulation show that the Adriatic Sea, as a whole, is a CO_2 sink with a mean annual flux of $36\,\mathrm{mg\,m^{-2}\,day^{-1}}$. The northern part absorbs more carbon ($68\,\mathrm{mg\,m^{-2}\,day^{-1}}$) due to an efficient continental shelf pump process, whereas the southern part behaves similar to an open ocean. Nonetheless, the Southern Adriatic Sea accumulates dense, southward-flowing, carbon-rich water produced on the northern shelf. During a warm year and despite an increase in aquatic primary productivity, the sequestration of atmospheric CO_2 is reduced by approximately 15 % due to alterations of the solubility pump and reduced dense water formation.

The seasonal cycle of temperature and biological productivity modulates the efficiency of the carbon pump at the surface, whereas the intensity of winter cooling in the northern sub-basin leads to the export of C-rich dense water to the deep layer of the southern sub-basin and, subsequently, to the interior of the Mediterranean Sea.

1 Introduction

Marginal seas play an important role in air-sea CO_2 exchange because of their intense biological activity (20 % of the ocean's primary production occurs in the continental margins) (Wollast, 1998). In addition, the backward flux of CO_2 to the atmosphere is prevented due to active transport processes (e.g. dense water formation) that enhance the vertical transport of carbon out of continental margins into the deep layers of the oceans (Carlson et al., 2001). However, the assessment of the contribution of marginal seas is typically based on the extrapolations derived from carbon budgets computed over a few seas or global estimates that describe marginal seas with inadequate spatial and temporal resolution. The extrapolation of fluxes from limited (in terms of the temporal and spatial coverage) datasets for systems generally characterised by intrinsically high spatial and temporal variability may cause large uncertainties in estimating of the role of marginal seas in the global carbon budget (Hofmann et al., 2011).

Therefore, the contribution of marginal seas to the exchange of CO_2 remains controversial (Chen and Borges, 2009), and acquisition of additional reliable estimates is an important step in the computation of the global carbon budget. The carbon sink for the world ocean is equal to 2.3 Pg C yr^{-1} (Le Quéré et al., 2009), and the contribution of the continental shelf seas is on the order of 10–20 % based on estimations of 0.45 Pg C yr^{-1} (Borges et al., 2005), 0.22 Pg C yr^{-1} (Cai et al., 2006), and, for the most recent study, 0.33–0.36 Pg C yr^{-1} (Chen and Borges, 2009).

Local studies investigating the mechanisms driving carbon sequestration in marginal seas as well as estimates of carbon fluxes at the regional scale can be important contributions to global carbon budget computations (Borges et al., 2006; Fennel and Wilkin, 2009; Prowe et al., 2009; Liu et al., 2010; Artioli et al., 2012). A modelling approach can help in exploring parameters that are difficult to measure during field campaigns, describing the appropriate processes at the local scale, and integrating theoretical knowledge and experimental information (Hofmann et al., 2011).

In this study, we analysed the role of the Adriatic Sea (AS), a marginal sub-basin of the Mediterranean Sea, in the global carbon cycle (Fig. 1). The AS is one of the most productive areas of the Mediterranean Sea (Mangoni et al., 2008) and is a site of intense dense water formation during the winter (Gačić et al., 2001). These features are constituent components of the continental shelf pump (CSP) process (Tsunogai et al., 1999), thus the AS is an area of efficient sequestration of atmospheric carbon to the interior of the Mediterranean Sea (de Madron et al., 2010).

The CSP process starts in the Northern Adriatic Sea (NA) on the continental shelf (a gently sloping shelf, oriented NW-SE). Nutrient input from the rivers (primarily from the Po River) sustains autotrophic production, which uses carbon that is taken up through air-sea exchange. Biological production is mainly confined to the western part of the NA where river input generates the density and trophic frontal system, known as the Western Adriatic Current (WAC) (Zavatarelli et al., 1995; Solidoro et al., 2008; Mozetič et al., 2009). The sinking of organic carbon and the horizontal transport of organic and inorganic carbon towards the south (off the shelf) and downward (into the deeper Central and Southern Adriatic sub-basins, CA and SA) are the mechanisms that prevent the flow of carbon back to the air-water interface.

In particular, the formation of dense water on the northern shelf in winter and its sinking and spreading southward sustain the downwelling of carbon-rich water masses. Furthermore, in the SA pit (a 1200 m deep area connected to the Mediterranean Sea through the Otranto Strait, Fig. 1), winter cooling causes deep convection in the open central part, which fertilises the photic layer (Gačić et al., 2002) and increases the volume of dense water (Manca et al., 2002) that accumulates in the SA pit. The sinking of organic carbon and the vertical mixing associated with deep convection contributes to the export of carbon to the deeper layers.

The AS has been the subject of several large-scale studies due to its economic and social importance (Arneri, 1996; Degobbis et al., 2000; Giani et al., 2005); however, a quantification of the carbon cycle has only been partially completed (de Mandron et al., 2010). The few available observations regarding the carbon system variables and processes (Lucchetta et al., 2010; Turk et al., 2010) do not exhaustively address the spatial and temporal variability of the AS and provide an incomplete estimate of the role of the AS in the Mediterranean carbon cycle. An estimate of the CO_2 exchange for the Mediterranean Sea has been computed based on satellite data (d'Ortenzio et al., 2008); however, this previous study used a relatively coarse resolution (0.5 × 0.5°) and covered only the SA.

Modelling studies that address the coupling of the carbon pump with the formation and spread of the dense water as well as the carbon budget of the AS are lacking. Previous modelling studies mainly focused on the temporal and spatial decoupling between nutrient cycles and the production, accumulation and consumption of organic matter (Polimene et al., 2007). Spillman et al. (2007) highlighted the effect of the various forcing mechanisms (e.g. Po River flow, local wind and temperature) in shaping the patterns of the trophic status in the north-western region of the AS.

The objective of this paper is to describe and quantify the mechanisms of the continental shelf pump in the Adriatic Sea and evaluate the interannual variability of the CO_2 sequestration rates using the results of a two year simulation. We compare two specific years (2007 and 2008) because they are characterised by remarkably different winter and summer weather conditions. The winter of 2008 was similar to the current climatic conditions, whereas the winter of 2007 was much milder. This difference allows for an estimate of the impact of specific climatic conditions on the formation and spreading of dense water (Querin et al., 2012), the continental shelf pump process, and the extent of air-sea CO_2 exchange.

This paper is organised as follows. In Sect. 2, we describe the model and the simulation configuration. In Sect. 3, relevant physical and biogeochemical dynamics and the validation of the model are presented along with a description of the CO_2 air-sea exchange in the Adriatic Sea. The mechanism of the carbon pump is discussed in the Sect. 4, which closes with an analysis of the carbon budget for the Adriatic Sea. The conclusions are presented in the last section.

2 Materials and methods

2.1 Site description

The Adriatic Sea is a temperate marginal sea characterised by an elongated shape (approximately 800 by 200 km) and an overall surface area of 380 000 km^2. Morphologically, the Adriatic Sea is composed of a shallow continental shelf in the northern part and a deeper pit (approximately 1200 m depth) in the southern part where the Otranto Strait connects the AS to the Mediterranean Sea (Fig. 1). The Po River, together with several other rivers located along the north-western coast, are the major sources of freshwater and nutrients (Cozzi and Giani, 2011).

2.2 Model description

The model simulation is performed using a three-dimensional, coupled physical-biogeochemical-carbonate model. The physical model is a customised version (Querin et al., 2006, 2012) of the MITgcm (Marshall et al., 1997) finite volume, non-hydrostatic, general circulation model. The biogeochemical model (Fig. 2), specifically developed for the Adriatic Sea (Cossarini and Solidoro, 2008), simulates the carbon and phosphorus cycles, where the latter is considered the limiting nutrient in the AS (Solidoro et al., 2009; Mozetič et al., 2009). The model is designed to reproduce the alternating prevalence of the classic food chain over the microbial food web as the dominant energy pathways in the marine ecosystem as a function of the environmental conditions (Cushing, 1989; Legendre and Rassoulzadegan, 1995). Diatom and mesozooplankton (Mzoo) groups are the compartments involved in the classic food chain, which comprises the highest primary and secondary production rates and drives carbon mainly towards the creation of particulate organic carbon (POC) and export production. Under more oligotrophic conditions, the microbial food web prevails, where the interaction between small phytoplankton (Nphy), small zooplankton (μzoo) and bacteria (bac) is sustained via the rapid recycling of nutrients, and the carbon cycle primarily involves dissolved organic carbon (DOC). Carbon and phosphorus dynamics in the particulate and dissolved organic compartments are uncoupled, and DOC accounts for only the labile component because the time scale of the simulation is relatively short. The carbonate model solves the carbonate system chemistry starting from the dissolved inorganic carbon (DIC) and alkalinity (OCMIP model already implemented in the MITgcm packages was used), whereas the air-sea CO_2 exchange processes are solved using the parameterisation by Follows et al. (2006). The DIC and dissolved oxygen are computed based on the consumption and production terms of the phytoplankton and bacteria functional groups, which also alter the alkalinity (Wolf-Gladrow et al., 2007). Other specific model features include rest and active phytoplankton respiration (as in Polimene et al., 2007), bacterial lysis as a function of oxygen availability and the dependence of alkaline phosphatase on the phosphorus availability (Hoppe, 2003; Labry et al., 2005).

Sediment dynamics are not explicitly included in the model formula. Remineralisation occurs for sinking material, and burial is computed as a fraction of the material that is sunk in the last layer of the water column.

Results of a sensitivity analysis of the biogeochemical model (Cossarini and Solidoro, 2008) was used to obtain an empirical calibration of the model and to set the parameters used in the numerical experiment.

2.3 Model configuration

The computational domain covers the AS north of the Otranto Strait (from latitude 40.3° N to 45.9° N) with a horizontal resolution of 1/32° (~ 3.4 × 2.4 km) and 51 unequally spaced levels along the vertical dimension (to a depth of 1230 m in the SA pit).

The lateral boundary conditions include the freshwater river and nutrient discharge and the exchange at the Otranto Strait. Daily runoff data of the Po River are derived from a hydrographic station (courtesy of A. Allodi – ARPA – SIM Area Idrologia – PARMA – Regione Emilia Romagna), whereas climatological data are used for the other 16 rivers. Nutrient concentrations at the Po River mouth are set equal to 0.06, 0.02 and 0.05 mg P l^{-1} for DIP, DOP and POP, respectively. These values are estimated using the dataset of Cozzi and Giani (2011) and the freshwater discharge rates. These values, which are only slightly lower than those proposed by Ludwig et al. (2009) for the Mediterranean rivers, are also used for the other Adriatic rivers.

The concentrations of alkalinity, POC and DIC at the river mouths are set equal to those observed at the closest coastal stations, as reported in recent datasets for the north-western area of NA (Solidoro et al., 2009; Lucchetta et al., 2010).

Initial conditions (ICs) and boundary conditions (BCs) for the velocity, salinity and temperature at the Otranto Strait are extracted from the 1/16° INGV operational model of the Mediterranean Sea (MFS – Mediterranean ocean Forecasting System – model, Tonani et al., 2008), whereas BCs for the biological and the chemical parameters are derived from the OPATM-BFM forecast model (Lazzari et al., 2009). BCs at the Otranto Strait and ICs for alkalinity are computed using the formula proposed by Schneider et al. (2007), whereas DIC is computed via the CO2SYS model (Lewis and Wallace, 1998) using temperature, salinity and alkalinity data and a pH value of 8.1.

Regarding the surface atmospheric forcing, high spatial and temporal resolution wind data are obtained from the atmospheric models ETA006 and ALADIN, whereas daily heat and evaporation-minus-precipitation fluxes are interpolated from the Mediterranean Forecast system (MFS) model (Querin et al., 2012). Atmospheric $p\mathrm{CO}_2$ is set as a constant equal to 380 ppm (Artuso et al., 2009).

3 Results

3.1 Weather conditions and physical dynamics

The simulation covers 2 yr (2007 and 2008) and is characterised by different winter conditions: 2008 is characterised by winter conditions similar to the last decadal climatology, whereas winter 2007 is much warmer with a mean positive total heat flux anomaly of 31 $\mathrm{W\,m^{-2}}$ with respect to the normal climatology (Fig. 3). As a consequence of this anomaly, the simulation shows reduced dense water formation in the NA continental shelf during 2007 (Fig. 3). Conversely, a large volume of dense water is observed in 2008 (as explained below), which sustains the continental shelf carbon pump in the Adriatic Sea. Querin et al. (2012) report that the dense water mass forms a sub-surface current that slowly sinks into the deeper layers of the CA and SA sub-basins. Figure 3 also shows the presence of a net positive heat flux anomaly during the summer of 2008, whereas the summer 2007 condition is similar to the normal climatology.

Because the efficiency of the continental shelf pump is controlled by specific winter conditions, the relative differences between the two selected years and the reference climatology can provide a qualitative insight into the possible consequences of different climatic scenarios on the carbon cycle of the AS.

3.2 Modelled ecosystem dynamics and comparison with data

The freshwater input from the NA rivers (the Po River and other contributors) generates a nutrient-rich current that flows southward along the Italian coast (WAC; Poulain et al., 2001). As a consequence, a frontal system and a strong west-to-east nutrient gradient are typical features of the NA (Zavatarelli et al., 1998; Solidoro et al., 2009). Within the WAC, DIP concentrations are within the range of 0.1–0.15 $\mathrm{mmol\,m^{-3}}$, whereas the DIP levels never exceed 0.05–0.07 $\mathrm{mmol\,m^{-3}}$ in the open sea (Table 1; see also Zavatarelli et al., 1998). The seasonal cycle shows higher DIP concentrations in the autumn and winter when mineralisation prevails over uptake and external inputs are higher. In contrast, lower DIP concentrations are observed during the spring and summer when biological uptake prevails (Table 1). Outside of the WAC area, the DIP profiles show an accumulation at the bottom during the spring and summer stratification (Table 1, and Solidoro et al., 2009). The model results reflect these recurrent features (Table 1) with a slight underestimation of the bottom DIP values in the off-shore area during the autumn. Of the two simulated years, 2008 shows higher surface DIP concentrations in the coastal area due to the greater riverine discharge compared to the previous year.

For the central (CA) and southern (SA) basins, the model simulates oligotrophic conditions (a DIP concentration less than 0.05 $\text{mmol}\,\text{m}^{-3}$) for the surface layer, whereas the deep layers of the CA and SA are characterised by DIP accumulation (concentrations greater than 0.1–0.15 $\text{mmol}\,\text{m}^{-3}$, Fig. 6, Table 1).

As a consequence of the nutrient availability, the model produces a chlorophyll *a* rich strip along the Italian coast (Fig. 4), which is a permanent feature that has been observed in satellite images (Barale et al., 2005) and reported in climatological descriptions of the area (Zavatarelli et al., 1998). The simulated chlorophyll *a* concentrations are consistent with the observed values (up to 2 $\text{mg}\,\text{m}^{-3}$) within the WAC (Zavatarelli et al., 1998; Mozetič et al., 2009; Bignami et al., 2007) and are usually less than 0.5–1 $\text{mg}\,\text{m}^{-3}$ in the centre of the basin (Solidoro et al., 2009; Del Negro et al., 2008). The productivity of this eutrophic coastal strip is nearly double that of the off-shore productivity (Table 1), and thus, the western region is the prominent zone for the biological carbon pump.

The maps show other important spatial patterns of surface chlorophyll *a*, such as the possible effects of the recirculation of the Po River waters toward the centre of the NA, which is driven by the northern gyre (Poulain et al., 2001) and induced by the bora winds. This circulation pattern contributes to the trophic north-to-south gradient along the continental shelf. As is commonly observed in satellite maps (Barale et al., 2005), the width of the WAC frontal system decreases in the southward direction, and other weaker recirculation patterns are also visible in the centre of the CA basin (Fig. 4).

The Southern Adriatic Sea is strongly oligotrophic with low levels of chlorophyll *a* and productivity (Fig. 4, Table 1). The contribution of the eutrophic WAC is weak and restricted to a narrow strip along the Italian coast, whereas input from the Neretva River and other south-eastern rivers trigger important local chlorophyll *a* signals in the Eastern Adriatic Sea (Fig. 4), as observed by Marini et al. (2010).

The open ocean convection driven by negative heat fluxes (Gačić et al., 2002) during the winter interrupts the oligotrophic condition of the SA. The convection causes deep mixing and nutrient upwelling that sustains a phytoplankton bloom in the centre of the pit (Santoleri et al., 2003; Batistić et al., 2011) according to a two-phase process (i.e. the "Gran Effect"; see Mann and Lazier, 1998). Model results (Fig. 5) show that during the first phase of intense vertical mixing, phytoplankton productivity is limited by the downward transport of phytoplankton biomass, and significant phytoplankton concentrations are simulated even at depths below the photic zone, as observed during sampling in February of 2010 (Batistić et al., 2011). Following the first phase, the upward flux of nutrients and the occurrence of thermal stratification trigger a surface bloom that has also been detected in satellite maps (Santoleri et al., 2003). The modelled blooms are dominated by diatoms (not shown), which is consistent with the experimental observations of Boldrin et al. (2002). As the summer stratification develops, a deep chlorophyll *a* maximum is reproduced by the model at depths of approximately 50 m (Fig. 5), which is also consistent with observational data (Boldrin et al., 2002).

3.3 CO_2 exchange at the air-sea interface

The simulated annual net CO_2 exchange in the three sub-basins of the Adriatic Sea (Table 2) indicates that the Adriatic Sea, in general, is a sink of atmospheric carbon (positive values in Table 2 indicate a flux from the atmosphere to the ocean). When considering the entire basin, a mean annual CO_2 exchange rate equal to 3.0 mmol C m^{-2} day^{-1} is observed, thereby indicating that the Adriatic Sea is slightly less efficient with respect to the uptake by temperate marginal seas (5.04 mmol C m^{-2} day^{-1}; Borges et al., 2005) or meso/eutrophic temperate continental shelf provinces (5.5 mmol C m^{-2} day^{-1}; Cai et al., 2006). However, the simulation shows a high spatial and temporal variability of the CO_2 flux; i.e. a strong south-north gradient (Table 2) and a marked seasonal variation (Fig. 6).

The highest CO_2 sequestration rate is simulated for the NA (Table 2) where the annual mean is similar to the uptake values reported for temperate marginal seas.

A value of up to 12 mmol m^{-2} day^{-1} (Fig. 6) is simulated during the coldest months when the pCO$_2$ in the upper layer decreases to approximately 200 µatm. Such a high sequestration rate is confirmed by measurements at one point in the northernmost part of the NA (Turk et al., 2010). The authors observed a strong seasonal trend in the CO$_2$ flux, with mean values varying from 0.9 to 12 mmol C m^{-2} day^{-1}, and determined that this variation was related to the effects of temperature on the CO$_2$ solubility and the influence of fresh river water that is undersaturated with respect to DIC.

CA and SA show mean CO$_2$ exchange rates of approximately 2.5 and 1.5 mmol C m^{-2} day^{-1}, respectively, and the two sub-basins become a source of CO$_2$ during the summer periods (see summer values in Fig. 7) with a maximum outgassing rate of −6 mmol C m^{-2} day^{-1}.

In the SA, the central region (i.e. the Southern Adriatic pit) has a mean CO$_2$ exchange rate of approximately zero, which is similar to those of the open ocean (Cai et al., 2006). Estimations that the SA can behave similar to an open ocean have been reported based on satellite-derived CO$_2$ flux data (d'Ortenzio et al., 2008). The mean annual estimates reported by d'Ortenzio et al. (2008) in the intervals of −0.7–0 and 0–0.7 mmol m^{-2} day^{-1} for pixels of 0.5 × 0.5° are comparable with the model estimates of 0.70 and 0.36 mmol m^{-2} day^{-1} for 2007 and 2008, respectively, for the central part of the SA. Conversely, both the western and eastern parts of the SA show a mean sink behaviour due to the local effect of the continental shelf pump induced by the biological productivity of the residual WAC (western part) and the river input (eastern part).

The evolution of the CO$_2$ exchange follows a clear seasonal cycle (Table 1 and Fig. 7) that is driven by the temperature-modulated CO$_2$ solubility and biological productivity. The CO$_2$ solubility is higher in the winter (water pCO$_2$ decreases to 250–200 ppm) and lower in the summer (water pCO$_2$ increases to greater than 450 ppm in SA). The north-to-south temperature gradient is responsible for differences in the CO$_2$ exchange rate among the sub-basins. The SA is generally 1.1 °C and 2.4 °C warmer than the NA in the summer-autumn and winter-spring, respectively (Querin et al., 2012), which corresponds to a mean decrease in the solubility of CO_2 of 4 % in summer-autumn and 8 % in winter-spring.

The effect of the ecosystem productivity that contributes to the undersaturation of CO_2 at the surface is higher in NA (Table 1) and strengthens the north to south negative gradient in the air-sea CO_2 flux (Table 2). The spatial differences in the biological productivity of the NA and CA (Fig. 4) drive the difference in the CO_2 uptake between the western and eastern parts of the sub-basins (Fig. 6). The western regions are generally 20–30 % and 5–10 % more efficient in absorbing atmospheric CO_2 in the NA and CA, respectively.

4 Discussion

4.1 Mechanisms driving the carbon pump in the Northern Adriatic Sea

The mechanism of the carbon pump in the NA involves the combined effects of DIC consumption by biological processes, CO_2 solubility and the formation and southward spread of dense water masses, which have been enriched in organic and inorganic carbon.

The numerical simulation shows that in the WAC region, an excess of organic production over respiration produces a depletion of DIC that strengthens the solubilisation of atmospheric CO_2 and promotes organic carbon production. Eventually, organic carbon is transported out of the shelf and partly buried in the continental shelf (Fig. 7). The largest unbalance between the consumption and production of DIC (i.e. net community production) occurs during the winter and spring when the productivity of the ecosystem is the highest (not shown). At this time, the system attains the highest difference between the actual concentration of CO_2 at the surface and its saturation, thereby driving a strong air-to-sea CO_2 flux (see Fig. 6).

The role of biological processes in controlling CO_2 concentration is highlighted by the fact that the local CO_2 concentration minima are observed in conjunction with the largest decoupling between production and respiration. Furthermore, the imbalance in the production and respiration is greater at the western side of the NA where the productivity of the system is higher. As a consequence, the concentration of CO_2 in the western side is lower, and the difference between the CO_2 concentration and saturation levels, as well as the air-to-sea CO_2 flux, are maximised.

The loss of carbon via burial accounts for approximately 1 % of the primary production; therefore, as reported by de Madron et al. (2010), a significant amount of organic carbon is advected southward.

Figure 7 shows that the slightly lower net community production in the winter of 2008 relative to 2007 (caused by a higher contribution of respiration) only marginally affected the differences in the CO_2 flux because the higher CO_2 saturation value in 2008 with respect to 2007 was the dominant effect.

The eastern region shows higher saturation values during the winter of 2008 due to the effect of stronger cooling in this area (which is the principal site of dense water formation; Querin et al., 2012). As a consequence, the eastern NA shows the highest difference in the CO_2 winter-spring flux between the 2 yr (+27 %, based on flux rates of 5.2 mmol C m^{-2} day^{-1} in 2007 and 6.6 mmol C m^{-2} day^{-1} in 2008).

During the summer, the system tends to become heterotrophic; i.e. respiration occurs at the same or greater level than production, and the DIC concentration in the water column increases (Fig. 7). Concurrently, the CO_2 saturation decreases due to an increase in the water temperature. In the eastern region, these two processes increase the CO_2 concentration up to or greater that the saturation level. When this occurs, the system can become a source of CO_2, as shown during the months of July and August of both studied years (Fig. 4).

4.2 Southward transport and sinking of dense, carbon-rich water masses

The biological enrichment of organic carbon in the western NA waters and the formation and fate of the dense water formed on the shelf lead to the sequestration of carbon from the surface. The cyclonic circulation of the NA and the slow downward flow along the continental slope transport the dense, carbon-rich waters toward the deeper zones of the CA and SA.

The southward transport of dense water is depicted by the sequence of plots for different timepoints (March, April and June) and various latitudes (Fig. 8). The plots capture the spread of a dense water flow of approximately 0.1 sv ($10^5\,\mathrm{m}^3\,\mathrm{s}^{-1}$; Querin et al., 2012) that cover a distance of approximately 1° per month. The comparison between the 2 yr aids in the understanding the quantitative effect of winter cooling and its impacts on the efficiency of the continental shelf pump.

During March of 2008 (Fig. 8b), the C-rich Adriatic dense water (AdDW, ρ greater than $1029.5\,\mathrm{kg\,m}^{-3}$) flows on the bottom of the slope, whereas during March of 2007 (Fig. 8a), the C-rich water layer is shallower and mainly confined to the western side of the slope. The organic carbon reaches the bottom mainly through the processes of sinking or diffusion. It is important to note that in 2008, the organic carbon content of the AdDW is 5–10 $\mathrm{mmol\,C\,m}^{-3}$ higher than that of the adjacent water masses and the water occupying the same depth during the previous year.

During the warmer conditions of 2007, both the downward currents flowing along the slope and the extent of carbon sequestration are much smaller.

The analysis of the other sections in the CA (Fig. 8c, d) and SA (Fig. 8e, f) regions shows that the AdDW is characterised by a lower density than that of the NA section due to the dilution with adjacent water masses. Furthermore, the POC concentration decreases via biological consumption due to respiration and degradation processes, which increase the DIC concentration.

The comparison between the 2 yr highlights the effect of different climatic scenarios on the role of dense water transport and the function of the continental shelf pump. In the CA region, a core of dense C-rich water lies at the bottom of the slope in 2008, whereas in 2007, C-rich water masses occupy the upper layers (Fig. 8c, d). Subsequently, a cascade of C-rich dense water was observed flowing into the SA pit in 2008 (Fig. 8f) but not in 2007 (Fig. 8e). As the C-rich dense water cascades into the southern

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pit, it becomes isolated from the surface, and a supersaturation of the DIC concentration in the deep layers can be observed.

The efficiency of the carbon sequestration is dependent on the properties of the vertical transport; i.e. a greater water density corresponds to a deeper flow and a larger amount of carbon that is moved away from the surface layer.

4.3 Deepening of the C-rich dense water below the mixed layer depth in the CA and SA

The effect of the deepening of the AdDW is assessed by computing the spatial mean of the vertical transport flux of inorganic and organic carbon over the western part of the CA and SA at 90 m depth and over the western and central parts of the SA at 190 m depth (Fig. 9). The spatial pattern of the vertical fluxes (sum of advection, diffusion and turbulent transport) is characterised by very high spatial variability. The mean vertical flux is generally close to zero as a result of the balance of positive and negative vertical terms. The mean vertical flux differs significantly from zero when the AdDW flows across surfaces resulting in a net downward flux of carbon-rich water.

In particular, across the 90 m surface of the CA (Fig. 9a), the fluxes are generally slightly upward (positive in the figure) because the deep layers are oversaturated in DIC (see also Carlson et al., 2001; Sarmiento and Gruber, 2006) and the turbulent regime affects the surface layer. The net flux becomes significantly negative only during the spring of 2008, as a result of the AdDW flow. At this time, the sum of the downward carbon fluxes is higher than the CO_2 exchange at the surface, and the downward flux is sustained by the lateral transport from the northern basin. The same phenomenon is much weaker in the spring of 2007 due to the negligible AdDW volume.

An additional term affecting the downward flux occurs when the sinking of particulate organic material is included, which accounts for approximately 50 mg C m^{-2} day^{-1} and increases during the winter-spring period. The importance of this flux decreases rapidly with depth. For example, at 180 m (the deepest part of the CA), this flux was reduced to 7 and 12 mg C m^{-2} day^{-1} in 2007 and 2008, respectively. It was later determined that the largest fraction of carbon entering the CA is transported southward to the SA. The AdDW enters the SA at an intermediate level and cascades along the Bari Canyon system (as described by Rubino et al., 2010; Querin et al., 2012) during June and July. This phenomenon can only be observed in 2008 (Fig. 9b, c). Furthermore, Fig. 9c shows that fluxes at 180 m are generally negative in the western part, and large downward fluxes are observed in the winter/spring of 2008. This is the result of the winter cooling over the narrow western shelf of the SA and the formation and sinking of the local dense water. Conversely, the fluxes across the central part of the SA (Fig. 9d) are generally positive (upward) to balance the downward lateral fluxes across the slope on both sides of the pit (only the western part is shown in Fig. 9c). A significant change in the central SA trend occurs concurrently with open ocean convection (winter 2008), which triggers a net downward transport of DIC and organic carbon to the interior of the SA. This process can be clearly observed in 2008 and lasts for two months (Fig. 9d), whereas the warmer winter condition in 2007 produces a less intense downward flux. Even if it occurs for a relatively short duration (a few days), the winter convection produces an increase in the CO_2 solubility and vertical mixing that induces the fertilisation of the surface layer, which prompts a subsequent phytoplankton bloom and sinking of organic matter to the central part of the SA (Fig. 6).

In particular, after the winter convection, the primary production can increase approximately by 100 % with respect to the mean values (Table 1), and the phytoplankton bloom lasts for nearly one month. At this stage, the sinking of organic carbon shows an increase of approximately +20–25 mg C m^{-2} day^{-1} at 90 m, and 10 mg C m^{-2} day^{-1} at 180 m (Fig. 9d).

However, only a small fraction of the organic production reaches the bottom since the largest part of the sinking organic carbon is respired within the water column. In fact, the simulated values of the sinking flux at 800 m depth decrease at 4 and 10 mg C m^{-2} day^{-1} for the post-bloom periods in 2007 and 2008, respectively. These values are highly similar to the observations reported by Boldrin et al. (2002), who measured values of 9.7 mg C m^{-2} day^{-1} at 150 m and 7 mg C m^{-2} day^{-1} at 1050 m depth during the post-open-ocean convection.

The deep convection has three effects: it triggers an important bloom that transforms surface DIC into sinking POC, it enhances the solubility of CO_2 by cooling the surface layer and it strengthens the accumulation of dense water in the deep layers of the SA pit. These three phenomena all contribute to an increase in the atmospheric CO_2 uptake by the sea (approximately +2.5 mmol C m^{-2} day^{-1} in March–April 2008, Fig. 4) and contributes to a reduction in the role of the SA as source of CO_2.

In the SA pit, the majority of sinking organic carbon is respired and mineralised within the water column, thereby contributing to a condition of DIC oversaturation in the deep layers, as typically observed in the open ocean (Carlson, 2001; Sarmiento and Gruber, 2006).

The water mass in the deep layers of the SA pit is very dense and oversaturated with respect to DIC (DIC > 2360 mmol m^{-3}) and constitutes the core of a deep outflow current (DWOC) that fuels the deep Mediterranean circulation, in accordance with the anti-estuarine circulation of the Adriatic Sea (Gačić et al., 2001). Therefore, deep SA water has a very relevant role in the long-term sequestration of carbon from the atmosphere. The DWOC is essentially baroclinic and depends on the integrated deep water production over the entire Adriatic Sea in the winter (Gačić, 2001). Thus, winter weather conditions control the continental carbon pump in the NA and, most importantly, the amount of dense water enriched in carbon that accumulates in the SA pit and can be advected to the deep layers of the Mediterranean Sea.

When the dense outflow current is weakened by warmer winter conditions, DIC-oversaturated water masses remain in the basin at an intermediate level and can be brought back to the surface during subsequent mixing events. The decrease in the CO_2 flux observed during the end of 2007–beginning of 2008 (Fig. 6) can be ascribed to the effect of the autumn mixing that precedes deep convection. The mixing raises the DIC-oversaturated water masses, which were not sufficiently deepened during the previous period.

4.4 Carbon balance of the Adriatic Sea

Regarding the carbon budget of the Adriatic Sea, the net CO_2 sink is estimated to be 1.74 and 1.66 $Tg\,C\,yr^{-1}$ for 2007 and 2008, respectively. Despite the significant impact of winter cooling in 2008 on the continental shelf pump, we observe an unexpected decrease in 2008. On the basin scale, the decrease in the second year is more evident in the CA and SA (−7 % and −25 %, respectively), whereas the NA shows a mean annual increase in the CO_2 sink of 4 %.

This unexpected result stems from the fact that the summer-autumn of 2008 is characterised by a significant increase in the total heat flux (+20 $W\,m^{-2}$) relative to the previous year with a warmer (1–1.5 °C) surface layer and lower (from −2 to −5 %) CO_2 solubility and CO_2 exchange rate (−0.4, −0.6 and −0.8 $mmol\,C\,m^{-2}\,day^{-1}$ in NA, CA and SA, respectively). The greater decrease is registered in the SA where the increase of surface temperature is the highest.

However, considering the different seasons of the 2 yr, we can calculate the effect of the climatic variability on the carbon pump in the Adriatic Sea.

When combining the results of the winter-spring of 2008 and the summer-autumn of 2007 (Table 1), which correspond to the typical climatological conditions, we obtain an estimate of the potential CO_2 sequestration for the AS of 1.84 $Tg\,C\,yr^{-1}$. However, combining the less favourable (in terms of the carbon sequestration) seasons of the 2 yr, i.e. the winter-spring of 2007 (+31 $W\,m^{-2}$) and the summer-autumn of 2008 (+9 $W\,m^{-2}$), the capacity of the Adriatic Sea to sequester CO_2 would be reduced to 1.56 $Tg\,C\,yr^{-1}$. The difference in the sinking role of the Adriatic Sea between these two modelled years (−15 %) shows the effect of a mean annual increase of 19 $W\,m^{-2}$ on the total atmospheric heat flux. These results show that interannual variability can potentially have an important effect for CO_2 flux estimation and that long term simulation and averages should be accounted for budget and compilation.

When all processes involved in the carbon budget of Adriatic Sea were considered, it was determined that input from rivers (of which the Po River and the northern rivers represent 75 % of the total discharge) is likely the most important term. The lateral total carbon input from rivers was calculated to be 2.3 Tg C yr^{-1} for 2007 and 2.9 Tg C yr^{-1} for 2008, which are 27 % and 40 % higher, respectively than the CO_2 air-sea exchange rates.

The BCs at the rivers are set using data for a coastal area near the Po River delta (Solidoro et al., 2009; Socal et al., 2008 for POC and DOC; Lucchetta et al., 2010 for DIC; Del Negro et al., 2008, Pugnetti et al., 2008 for the biological compartments). Using these data, we assume that 90 % of the carbon from the river input was in the form of DIC (this estimate is just slightly greater (10 %) than that proposed by Ciais et al., 2008 for Southern European rivers).

These values refer to the fluxes that reached the open sea (as suggested by Ciais et al., 2008) without taking into account the entire terrestrial load and the role of deltas and estuaries, which are considered important consumers of terrestrial organic carbon and sources of CO_2 (Chen and Borges, 2009; Ciais et al., 2008) and require specific modelling of estuary processes. These data suggest that the terrestrial input should be considered, and river-sea exchange rates should be estimated.

In the two simulated years, burial accounted for 0.1 and 0.15 Tg C yr^{-1}. The process is stronger in the northern shelf and along the Northern Italian coast where it can comprise up to 5 % of the water column integrated primary production. Relatively high values are also simulated in the CA pit, where lateral transport from the western slope contributed to the accumulation of organic matter in this 230 m deep pit. However, the results of the simulation show that the largest component of the imbalance of the carbon budget is accumulated in the SA (which represents more than 76 % of the volume of the Adriatic Sea) and is exported toward the Ionian and Mediterranean seas. Our simulation shows net outward POC fluxes of 0.2 and 0.4 Tg C yr^{-1} and net outward DIC fluxes of 3.2 and 4.8 Tg C yr^{-1} in the two simulated years.

This study represents the first estimate of exchange fluxes at the Otranto strait based on model simulations. Previously, de Madron et al. (2010), using data from Civitarese et al. (1998), reported a net inward flux of POC of 0.19 Tg C yr^{-1}. It should be noted that the fluxes at Otranto have a complex three-dimensional structure (Cousman-Roisin et al., 2001) and a strong interannual variability, even within a decadal timescale (Civitarese et al., 2010), that can significantly influence the direction and magnitude of the fluxes.

Furthermore, it must be noted that given the large volume of the SA, the local accumulation of organic matter or DIC can occur even during short simulations due to physical processes. These terms can greatly exceed the surface air-sea exchange. Thus, long-term simulations are needed to obtain reliable estimates of the exchanges at the Otranto Strait and the relationship between the Adriatic Sea and the Mediterranean Sea carbon cycle. However, in such simulations, other processes should be included in the structure of the model (i.e. the dynamics of refractory DOC that constitutes a large pool of carbon, calcium-carbonate precipitation and dissolution dynamics, and the interaction of the pelagic environment with the sediment, Hofman et al., 2011).

5 Conclusions

In this study, the carbon cycle of the Adriatic Sea, a marginal basin of the Mediterranean Sea, is investigated using a coupled transport-carbonate-biogeochemical model.

The model simulation provides a description of the carbon cycle, which would be difficult to observe directly, and reveals that the Adriatic Sea is a sink for atmospheric CO_2 with a mean annual uptake (during the simulated time period) of $36\,\mathrm{mg\,C\,m^{-2}\,day^{-1}}$. However, the dynamics of the carbonate system are complex, and the spatial and temporal variability is high. The air-sea exchange is the result of the balance of the temperature-induced solubility pump, the biological carbon pump and the formation and spreading of winter dense water.

Temperature-induced solubility drives strong and seasonally variable air-sea CO_2 fluxes and causes remarkable latitudinal gradients. The continental shelf pump is active in the northern part of the Adriatic Sea and is caused by the high biological production fuelled by river fertilisation and the intense formation of winter dense water. In contrast, the central and southern regions are less productive and are warmer and negative (toward the atmosphere) CO_2 air-sea fluxes occur during summer.

The winter dense water formation in the northern continental shelf, as well as its spreading and sinking along the slope and into the deeper layers of the central and southern basins, are the key processes for sequestering C-rich water masses and preventing carbon re-exposure at the surface during the subsequent mixing period.

Winter open ocean convection in the southern pit enhances the storage of dense, C-rich water in the deepest layers.

The interannual variability of the winter conditions affects the strength of the solubility pump and the intensity and volume of the dense water reaching the deep layers of the southern pit. Because the C-rich, dense water of the deep layers fuels the deep Mediterranean Sea circulation, climate change would potentially decrease the capacity of the Adriatic Sea to absorb atmospheric CO_2. Considering the warmer seasons of the two simulated years, a potential 15 % reduction of the efficiency of CO_2 carbon sequestration was estimated due to an increase in the total heat fluxes. Finally, the simulation indicates the existence of important year-to-year feedback processes, thereby demonstrating the need for long-term studies to fully quantify the carbon budget for this marginal sea.

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Table 1. A comparison between the model results and observations for variables and relevant ecosystem processes. Values report mean and stardard deviation or range of variability. Sources of data: (1) Solidoro et al., 2009; (2) Zavatarelli et al., 1998; (3) Pugnetti et al., 2006; (4) Giordani et al., 2002.

	Zone	Period	Model 2007	Model 2008	Observation	Source
PO_4 [mmol P m^{-3}]	NA within the WAC surface	Win-Aut	0.25 ± 0.04	0.31 ± 0.11	0.38 ± 0.27	1
		Spr-Sum	0.17 ± 0.04	0.22 ± 0.05	0.11 ± 0.08	
	NA offshore surface	Win–Aut	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.03	1
		Spr–Sum	0.01 ± 0.01	0.01 ± 0.01	0.04 ± 0.02	
	NA offshore bottom	Win–Aut	0.05 ± 0.01	0.04 ± 0.01	0.08 ± 0.04	1
		Spr–Sum	0.06 ± 0.01	0.05 ± 0.01	0.05 ± 0.02	
	CA surface	Win–Spr	0.03 ± 0.03	0.04 ± 0.04	0.07 ± 0.03	2
		Sum–Aut	0.03 ± 0.03	0.03 ± 0.03	0.06 ± 0.060	
	SA surface	Win–Spr	0.04 ± 0.03	0.05 ± 0.04	0.06 ± 0.06	2
		Sum–Aut	0.02 ± 0.03	0.02 ± 0.03	0.05 ± 0.06	
	SA deep water	Win–Spr	0.11 ± 0.01	0.13 ± 0.01	0.08 ± 0.07	2
		Sum–Aut	0.14 ± 0.02	0.17 ± 0.03	0.10 ± 0.10	
Primary Production mg C m^{-2} d^{-1}	NA within the WAC	Annual	370 ± 150	335 ± 170	356–575	3
	NA offshore WAC	Annual	232 ± 71	245 ± 108	164–246	3
	SA pit	Annual	229 ± 141	230 ± 148	265	4
Sink of organic carbon mg C m^{-2} d^{-1}	CA central pit at 180 m	Annual	14.0 ± 5.0	43.6 ± 11.6	15.7	4
Burial mg C m^{-2} d^{-1}	CA central pit at the bottom	Annual	2.7 ± 0.9	4.1 ± 1.3	1.9	4

Table 2. Carbon exchange rates (mmol CO_2 m^{-2} day^{-1}) at the air-water interface for the three sub-basins during the two simulated years. The presented values are the annual, winter-spring and summer-autumn averages. Positive values indicate that the ocean acts as a CO_2 sink.

	NA (36 783 km^2)			CA (40 294 km^2)			SA (51 484 km^2)		
	annual	win-spr	sum-aut	annual	win-spr	sum-aut	annual	win-spr	sum-aut
2007	5.6	7.7	3.6	2.7	4.2	1.1	1.6	2.7	0.5
2008	5.8	8.4	3.2	2.5	4.6	0.5	1.2	2.8	–0.3

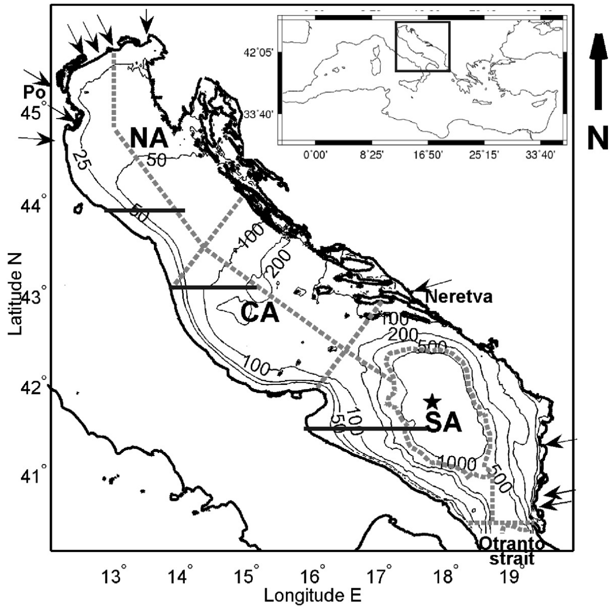

Fig. 1. A coastal and bathymetric map of the Adriatic Sea. The Otranto Strait, the major rivers (arrows) and the positions of three transects (black lines) and a station in the southern sub-basin (star) are shown. The northern (NA), central (CA) and southern (SA) sub-basins, the western (W) and eastern (E) subdivisions of the NA and CA, as well as the western, eastern and central (PIT) subdivisions of the SA, are delimited by bold grey dashed lines.

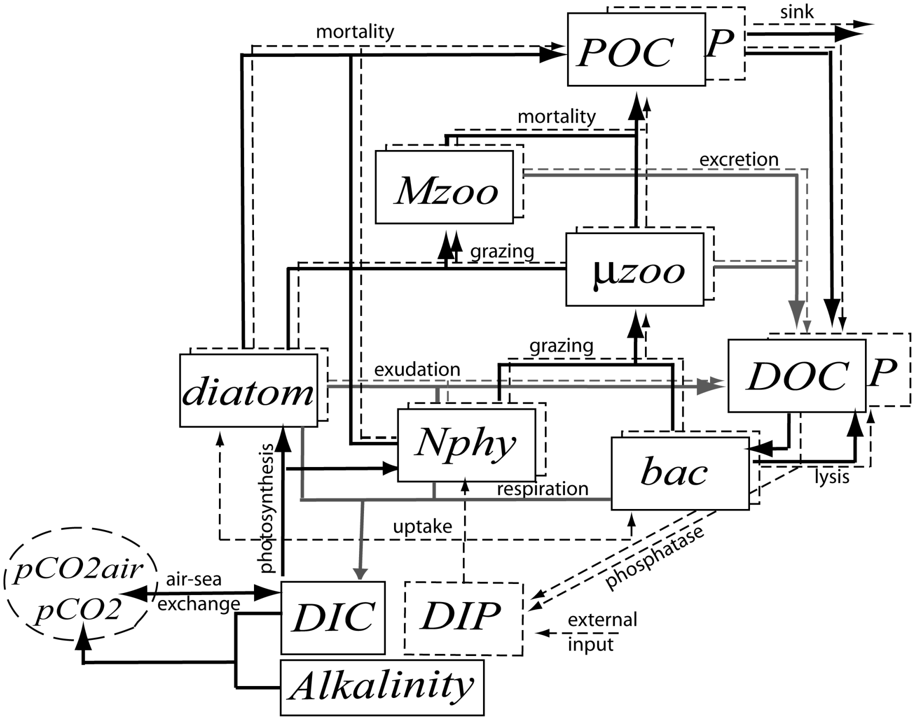

Fig. 2. A schematic of the biogeochemical model. Boxes and arrows indicate state variables and the fluxes of carbon (solid lines) and phosphorus (dotted lines), respectively.

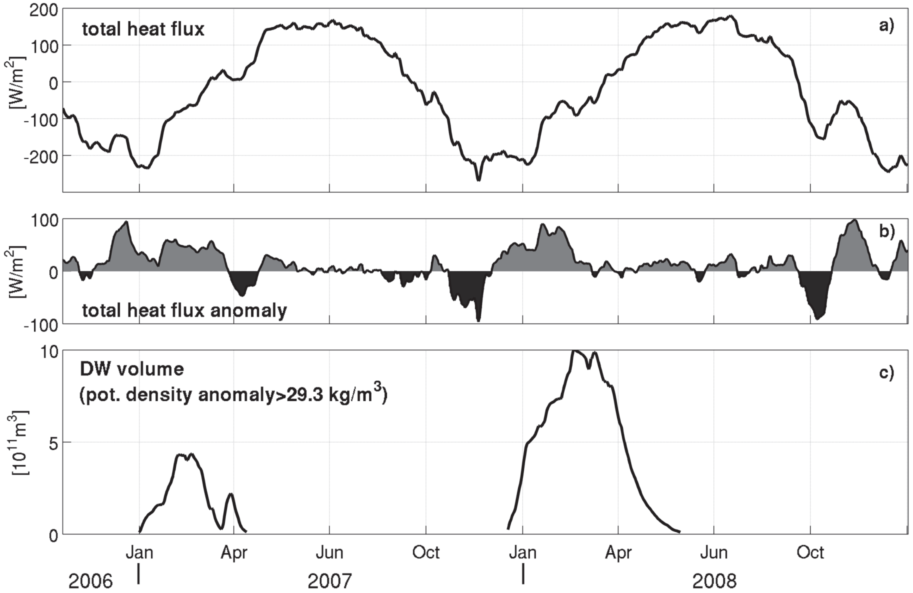

Fig. 3. The evolution of the total heat flux in the NA **(a)**, the anomaly with respect to the 2000–2010 climatology **(b)**, and the evolution of the volume of water with a density greater than 29.1 kg m^{-3} in the NA **(c)**.

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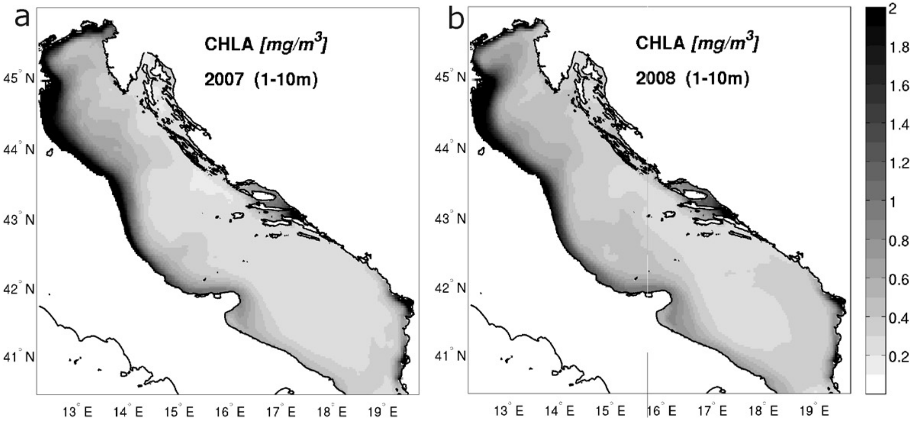

Fig. 4. Maps of the mean annual surface chlorophyll *a* concentration (mean of the upper 10 m) for 2007 **(a)** and 2008 **(b)**.

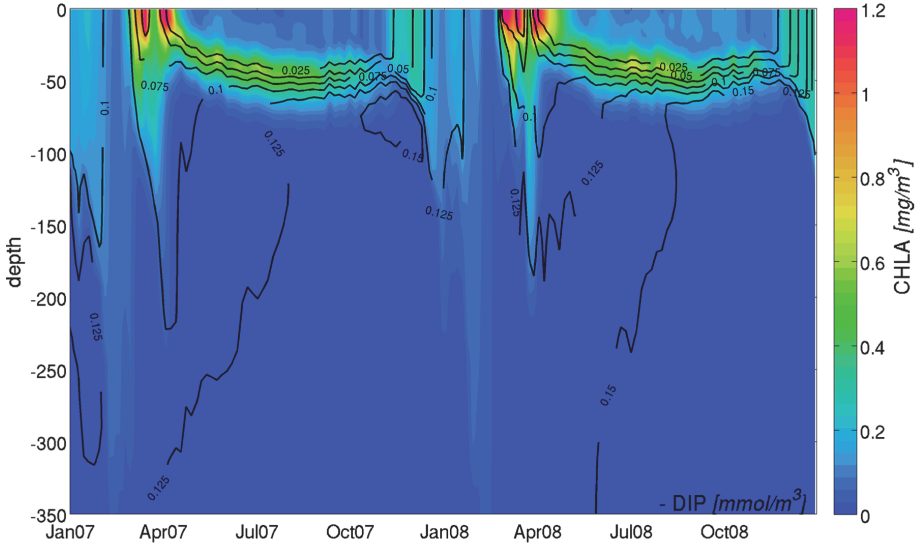

Fig. 5. Hovmöller diagram of chlorophyll *a* (shaded plot) and DIP (contour plot) in a station of Southern Adriatic pit (see star-point in Fig. 1).

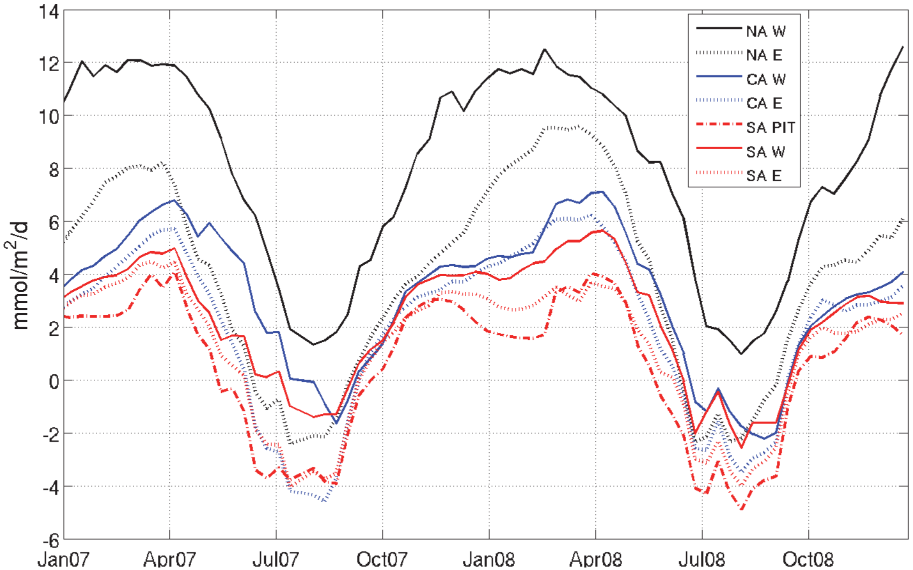

Fig. 6. Changes in rate of CO_2 exchange at the air-sea interface over time for selected sub-basins of the Adriatic Sea (see Fig. 1 for a definition of the sub-basins). Positive values indicate that the ocean acts as a CO_2 sink.

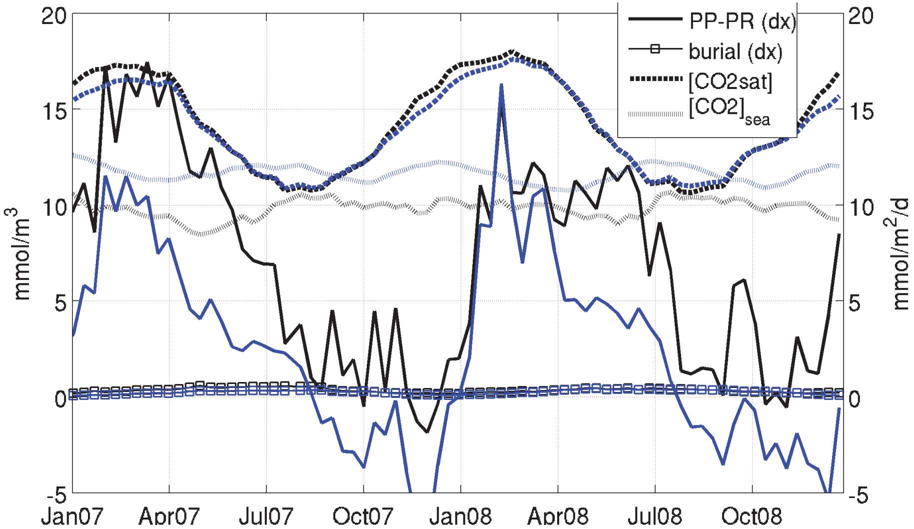

Fig. 7. Evolution of the vertically integrated (1–80 m) net primary production (gross primary production – total plankton respiration), bottom burial, CO_2 saturation and CO_2 concentration at the surface layer in the western (black lines) and eastern (blue lines) parts of the NA.

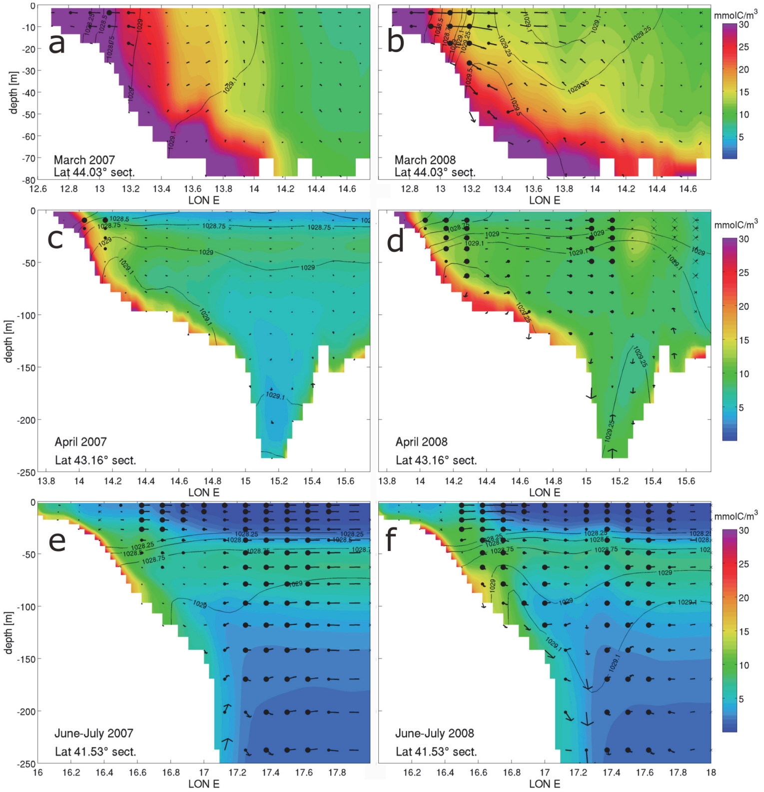

Fig. 8. Distribution of POC (filled contour) and density (isolines) in the 44.03°, 43.16° and 41.53° latitude sections (see position on Fig. 1). The average data from March, April and 15 June to 15 July for the three sections are presented. Arrows indicate the zonal-vertical components of the velocity (vertical velocities are amplified). The northward (cross) and southward (dot) velocities are reported for the absolute intervals 0–0.02 (small symbols), 0.02–0.04 (medium symbols) and > 0.04 m s^{-1} (large symbols).

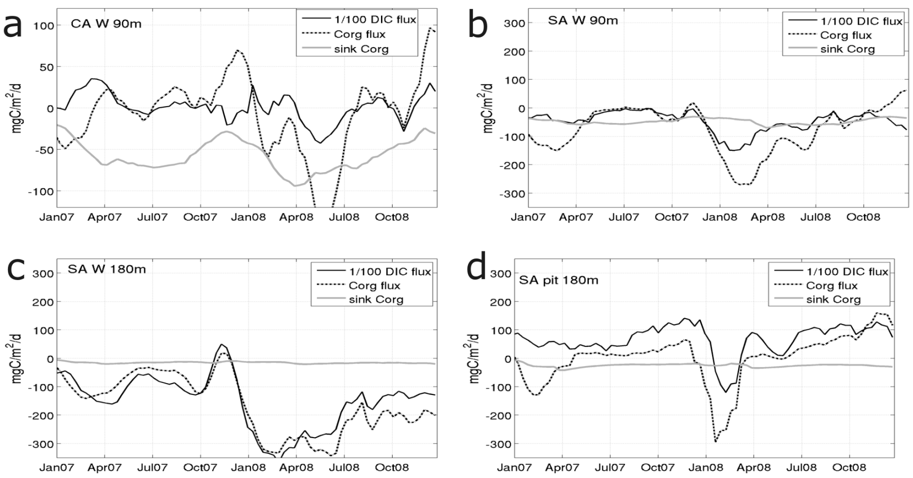

Fig. 9. Vertical transport (sum of the advection, diffusion and turbulent transport) of DIC and organic carbon and the sinking of organic carbon: the western part of the CA at a depth of 90 m **(a)**, the western part of the SA at 90 m **(b)** and 180 m **(c)** and the central part of the SA at 180 m **(d)**. Positive values indicate an upward flux.