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Air–sea CO_2 exchange in the Southern Adriatic Sea: assessing its role as a moderate carbon sink over the last decade

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Abstract

Coastal waters contribute significantly to the total oceanic carbon uptake. In this context, the cumulative influence exerted by marginal seas may be conspicuous. However sparse and unevenly distributed observations in such regions pose a serious limit to an accurate, experimentally based quantification of carbon dynamics. The Southern Adriatic (SAd) is one of the key sites of the Mediterranean Sea where open-ocean deep water formation occurs, a process recognized as a major driver of carbon sequestration. However, only a limited number of studies have investigated surface carbon dynamics and quantified air-sea carbon flux in the SAd. In this study, a newly validated, decade-long (2015-2024) high-resolution time series of CO_2 and hydrographic measurements collected at the EMSO-E2M3A South Adriatic observatory, located at the center of the Southern Adriatic Pit, has been analysed. The results showed that seasonal temperature variability and winter convection were the main processes driving the dynamics of surface partial pressure of CO_2 (pCO_{2sw}). Air–sea CO_2 flux (FCO_2), derived from in situ observations, indicated a clear seasonal pattern, with the SAd acting as a CO_2 sink during winter and as a source during summer. Importantly, the results revealed that the SAd acted as a moderate carbon sink over the last decade. Uncertainty analysis in the flux estimates were also evaluated, revealing that wind speed input data used for FCO_2 calculations influenced the magnitude of FCO_2. Finally, the results presented here showed how time series such as the SAd dataset can serve as critical assets for validating operational ocean models, such as the EU Copernicus Marine Service for the Mediterranean, by helping to identify discrepancies in the simulation of key processes.

1. Introduction

In the decade 2014-2023 it is estimated that the ocean has absorbed 10.5 $GtCO_2$ on average each year, which corresponds to around 26% of total CO_2 emissions (Friedlingstein et al., 2025). The concentration of carbon dioxide (CO_2) in the atmosphere has increased from approximately 278 parts per million (ppm) at the beginning of the Industrial Revolution (Gulev et al., 2021), to more than 421 ppm at the end of 2024 (Lan et al., 2024). This has led to an increasing ocean carbon uptake, which, in turn, has

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caused changes in seawater chemistry. The exchange of CO_2 across the air-sea interface is driven by the difference between the partial pressure of CO_2 in the seawater (pCO_{2sw}) and in the atmosphere (pCO_{2atm}). The CO_2 absorbed by the ocean reacts with seawater to form carbonic acid (H_2CO_3), much of which dissociates releasing hydrogen ions (H^+), bicarbonate (HCO_3^-), and, to a lesser extent, carbonate ions (CO_3^{2-}) according to the salinity, pressure and temperature dependent equilibrium constants (Zeebe & Wolf-Gladrow, 2001). The increased concentration of hydrogen ions causes a reduction of pH and of carbonate ions in seawater. This process is commonly referred to as ocean acidification (Doney et al., 2009; Gattuso and Hansson, 2011) and is one of the major threats to many marine organisms. Carbonate ions are an important building block of structures such as sea shells and coral skeletons. Decreases in carbonate ions can make building and maintaining shells and other calcium carbonate structures more difficult for calcifying organisms such as shellfish, corals and calcareous plankton (e.g., Ilyina et al., 2009; Lohbeck et al., 2012; Meyer and Riebesell, 2015) putting on risk the entire food web.

Global estimates of ocean carbon flux rely on both observations and models (Gruber et al., 2023; Friedlingstein et al., 2025). Many efforts have been made by the scientific community to increase the number and availability of carbon measurements from different sources (e.g., from research vessels, autonomous sensors, Argo floats) into quality controlled and openly accessible data products, resulting in more than 30 million observations in the Surface Ocean CO_2 Atlas (SOCAT) V2022 release. However, these observations cover only a small fraction of the ocean surface and the amount of new observations per year in the open ocean has decreased since 2017 (Bakker et al., 2023). Ocean reanalyses have demonstrated significant potential in bridging observational gaps by providing comprehensive, three-dimensional, basin-wide datasets that enable the investigation of spatial and temporal variability across multiple scales (Cossarini et al., 2021). However, generating a coupled physical-biogeochemical reanalysis remains a complex challenge (Park et al., 2018), due to uncertainties in the representation of interactions between physical and biogeochemical processes, the limited availability of biogeochemical observations for both data assimilation and validation, and the multivariate nature of the biogeochemical system, which involves intricate relationships between observed and modeled variables (Cossarini et al., 2021). As a result, models still struggle to accurately represent sparsely sampled regions, and considerable uncertainties persist, particularly in marginal and coastal seas (Resplandy et al., 2024). Despite their small size (about 7% of the global ocean area), marginal and coastal seas have a significant impact on the carbon cycle (Lee et al., 2011; Kapsenberg et al., 2017; Laruelle et al., 2018; Hassoun et al., 2019; Resplandy et al., 2024). The latest estimates from Roobaert et al. (2024) quantified the global coastal CO_2 flux equal to -2.2 $GtCO_2\ yr^{-1}$ (-0.6 $PgC\ yr^{-1}$) which represent around 21% of the total current CO_2 flux from the atmosphere to the ocean (10.5 $GtCO_2$; Friedlingstein et al., 2025). The seawater carbonate system in these regions is driven by complex interaction between physical and chemical processes, like the overturning circulation, ocean mixing,

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freshwater inputs and biological processes. These interactions vary over time and space highlighting the importance of sustained time series observations to better understand and separate their individual contributions (Garcia-Ibañez et al., 2024). Thus, in situ observations are of paramount importance to provide high spatiotemporal resolution in specific areas of interest, to monitor Essential Ocean Variables (EOVs), to inform about ocean conditions throughout the water column (Schroeder et al., 2022) and to assess the quality of different model products and satellite measurements.

The Mediterranean Sea is a semi-enclosed basin, where Atlantic Ocean water is exchanged through the Strait of Gibraltar and is one of the areas where CO_2 estimations remain sparse and unevenly distributed (Hassoun et al., 2022). Here, two major overturning circulation cells contribute to transporting carbon from the surface to the ocean interior (Lee et al., 2011). In the eastern Mediterranean, the northern and southern Adriatic play a key role in sustaining the thermohaline circulation (Robinson et al., 2001) and in capturing and storing CO_2 in the deeper layers (Cantoni et al., 2016; Ingrosso et al., 2017; Urbini et al., 2020; Cantoni et al., 2024). In particular, the Northern Adriatic Deep Water (NAdDW) represents the densest and most CO_2-rich water mass in the region, significantly contributing to deep ventilation and carbon sequestration in the eastern Mediterranean basin.

In this study, a new validated in situ time series of sea surface observations from the EMSO-E2M3A South Adriatic regional facility and ICOS ERIC observatory (nominal position 41.5053°N, 18.0806°E), hereafter EMSO-E2M3A, is presented. Time series of sea water partial pressure of CO_2 (pCO_{2sw}, µatm), hydrography and estimated CO_2 flux (FCO_2, mmol m^{-2} day^{-1}) are discussed. One of the major goals of this research is to assess the role of the southern Adriatic (SAd) as a carbon sink or source in the last decade. To our knowledge, this is the first time that a comprehensive study on carbon dynamics and carbon flux in the region using high resolution in situ observations has been achieved. Further, it is shown how the SAd pCO_{2sw} and FCO_2 time series can be a key asset for biogeochemical reanalyses. Considering the Mediterranean Copernicus Marine Service biogeochemical reanalysis, the SAd data allowed to validate the biogeochemical reanalyses as a good tool to represent local dynamics while highlighting the presence of some differences in the amplitude of seasonal cycles of both pCO_{2sw} and FCO_2.

The paper is organized as follows. Section 2 describes the study area, Section 3 describes the data used and the thermodynamic calculation performed to estimate carbon flux. Results are presented and discussed in section 4. Conclusions are provided in Section 5.

2. Study area

The southern Adriatic (SAd) is located between the Palagruža Sill and the Strait of Otranto, where maximum depth reaches about 1250 m in the Southern Adriatic Pit (SAP; Figure 1). This area is featured by a quasi-permanent cyclonic circulation, and it is well known that dense water formation takes place at the centre of the gyre through open-ocean convection (Ovchinnikov et al., 1985; Gačic et al., 2002;

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Mantziafou and Lascaratos, 2004; Chiggiato et al., 2016; Amitai et al., 2021) contributing to the eastern Mediterranean thermohaline circulation (Robinson et al., 2001).

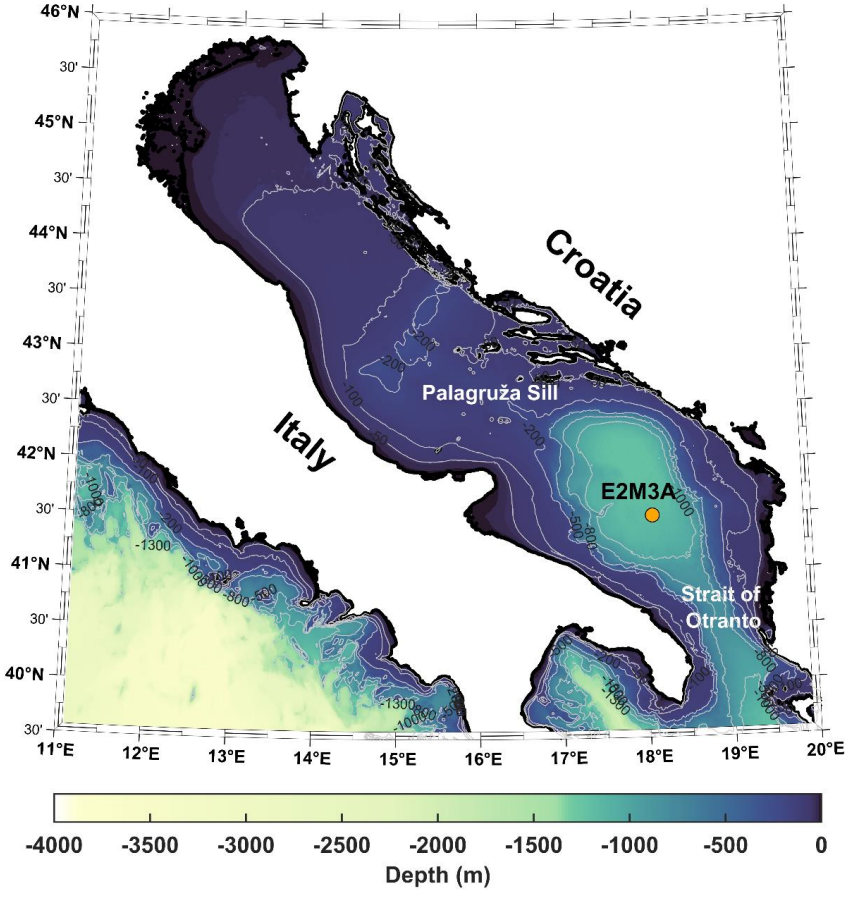

Figure 1. Map of the study area. The location of EMSO-E2M3A (nominal position 41.5053°N, 18.0806°E) moored at the center of the SAP is shown by the orange dot. The geographical boundaries of the southern Adriatic, i.e., the Palagruža Sill and the Strait of Otranto, are also displayed and highlighted by the two red lines.

The variability of physical and biogeochemical processes, including ocean carbon dynamics, is related to the interaction of different water masses (Civitarese et al., 2023). The Adriatic Dense Water (AdDW) occupies the bottom layer of the SAP and represents the main component of dense water for the whole Eastern Mediterranean basin (Schlitzer et al., 1991; Roether and Schlitzer, 1991). About 82 % of this water mass is formed through winter convection in the SAd (Ingrosso et al., 2017), while the remaining part has its origin on the northern Adriatic shelf and in the middle Adriatic Sea (Ovchinnikov et al.,

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1985; Bignami et al., 1990; Malanotte-Rizzoli, 1991). The Northern Adriatic Dense Water (NAdDW) is formed in the shallow northern Adriatic during winter, due to the cooling of the entire water column and of the evaporation caused by E-NE wind (named Bora). The process of formation of NAdDW is characterised by a high interannual variability as it is preconditioned by periods of low freshwater discharge by the rivers at least 4-5 months before its generation (Vilibić and Supić, 2005). These meteorological and oceanographic conditions also favour CO_2 and O_2 dissolution when surface water is undersaturated with respect to the overlying atmosphere. The CO_2 and oxygen enriched NAdDW is usually partially filling the middle Adriatic Pit and partly flows southward to the SAP (Cardin et al., 2011). On an interannual time scale, the physical and biogeochemical dynamics of the SAd is also strictly linked to that of the Ionian Sea (IS) by means of the Bimodal Oscillating System (BiOS). This mechanism changes the vorticity of the North Ionian Gyre (NIG) from cyclonic to anticyclonic and vice versa (Gačić et al., 2010; Civitarese et al., 2010; Civitarese et al., 2023). When the NIG is anticyclonic, the Modified Atlantic Water (MAW) coming from the Sicily Channel is in part deviated toward the northern Ionian and eventually enters the SAd, decreasing the salinity and the density of the AdDW. The change in the properties of the outflowing AdDW causes a progressive weakening of the anticyclonic upper-layer circulation in the IS. The circulation reverses, modifying the pathways of the water masses suppressing the northern branch of the MAW flow and favours the rapid advection of salty Levantine and/or Cretan Intermediate Water (LIW; CIW) along the eastern flank of the IS into the SAd. This results in an increase in the salinity (and density) of AdDW outflowing into the IS that gradually impairs the cyclonic NIG, eventually reversing it to an anticyclone. Finally, along the western coast in the SAd, the Adriatic Surface Water (AdSW) can be found. This is a relatively fresh and warm water mass, which originates from the northern Adriatic rivers runoff and flows southward along a narrow coastal layer of the western Italian shelf and exits through the Strait of Otranto.

The variability of the biogeochemical properties and the carbonate system of the SAd were almost continuously monitored by open ocean observatories, sampling activities and by ocean Argo floats and gliders. Particularly, the EMSO-E2M3A, which is located at the center of the SAP (Figure 1) and it is operated by the Italian National Institute of Oceanography and Applied Geophysics (OGS), represents a key research infrastructure to study biogeochemical and hydrographical properties of the whole water column in the SAP. EMSO-E2M3A is part of the European Multidisciplinary Seafloor and water column Observatory (EMSO) and the ICOS (Integrated Carbon Observation System) ERIC networks. It consists of a system of two moorings, with the main mooring housing the surface buoy and it is equipped with a meteorological station and radiometers, sensors for physical (hydrography) and chemical variables (pCO_{2sw}, dissolved oxygen and pH), telemetry and services (Ravaioli et al., 2016). The secondary mooring line is composed of an instrument chain with sensors at different depths for physical and chemical measurements from the seafloor to the intermediate layer (Cardin et al., 2025a). The station has been in operation almost continuously since 2006 and is the longest open sea time series in the Adriatic.

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3. Data and Methods

3.1. In situ measurements

The time series of pCO_{2sw} and hydrological variables presented in this study were measured by different sensors at the EMSO-E2M3A (Cardin et al., 2025b). A ProOceanus CO_2 sensor provided autonomous high-frequency (every four hours) measurements of pCO_{2sw} (µatm) from 2015 to 2024 with declared accuracy of ± 5 µatm. Hourly sea surface temperature (SST, °C), salinity (Sal) and dissolved oxygen (DO, µmol kg^{-1}) were measured by a SeaBird SBE 37-ODO with declared accuracy of ± 0.002 °C, ± 0.003 mS cm^{-1}, ± 0.1 % full scale range, respectively. DO from SBE 37-ODO was also used to calculate the apparent oxygen utilization (AOU, µmol kg^{-1}). This value corresponds to the difference between the equilibrium saturation of oxygen concentration in seawater with the same physical and chemical properties and the measured oxygen concentration, providing an estimation of the balance between primary production and respiration. AOU has been computed using the solubility coefficients from Benson and Krause (1984) as fitted by Garcia and Gordon (1992). A detailed description of the dataset used here and the quality control procedures applied to the data are available in Dentico et al. (2025).

To calculate air-sea FCO_2, hourly atmospheric molar fraction of CO_2 (xCO_2, ppm) from the ENEA Station for Climate Observations on the island of Lampedusa (Marullo et al., 2021; di Sarra et al., 2025) were used. Indeed, atmospheric pCO_2 measurements (pCO_{2atm}, µatm) at EMSO-E2M3A only started in December 2023, when a ProOceanus CO_2-Pro ATM was deployed allowing continuous measurements of both pCO_{2sw} and pCO_{2atm} in alternating mode. As in situ observations of pCO_{2atm} were not long enough to match with pCO_{2sw}, Lampedusa data was chosen as it represents one of the longest oceanic time series of pCO_{2atm} in the Mediterranean sea. Moreover, these data have been used in similar studies to compute FCO_2 at Mediterranean scale (e.g., Martellucci et al., 2024a; 2025) and in the northern Adriatic Sea (e.g., Urbini et al., 2020; Cantoni et al., 2024). From Lampedusa xCO_2 (indicated as xCO_{2_LMP}), the pCO_{2atm} relative to the local physical and atmospheric condition at EMSO-E2M3A (indicated as pCO_{2atm_E2M3Ar}) was calculated according to Weiss et al., (1974):

$$pCO_{2atm\_E2M3Ar} = xCO_{2\_LMP}\,(P - pH_2O) \quad (1)$$

where P is the air pressure (mbar) measured at EMSO-E2M3A and pH_2O (mbar) is the water vapour saturation that has been calculated according to Weiss and Price (1980):

$$pH_2O = Aexp^{(B - C(100/SST) - Dlog(SST/100) - E(SSS))} \quad (2)$$

where SST is sea surface temperature (K), SSS is sea surface salinity both measured at EMSO-E2M3A and the coefficients A, B, C and D can be found in Weiss and Price (1980). To assess the potential bias

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of using xCO_{2_LMP} for the calculation of CO_2 air-sea flux in the SAd, a comparison between pCO_{2atm} measured by the ProOceanus CO_2-Pro ATM sensor installed at EMSO-E2M3A (pCO_{2atm_E2M3A}) with pCO_{2atm_E2M3Ar} was performed. This comparison was limited to a four-month period between December 2023 and March 2024, when the CO_2-Pro ATM sensor was operational. The two time series show good overall agreement, however the differences tend to be larger at higher pCO_{2atm} values, while they remain smaller at lower values (Fig. S1, S2a, Supplementary Material). A mean difference of +2.67 ± 3.15 µatm between pCO_{2atm_E2M3A} and pCO_{2atm_E2M3Ar} indicate that pCO_{2atm_E2M3A} is on average higher than pCO_{2atm} derived from xCO_{2_LMP}. A detailed investigation of the reasons behind this difference was beyond the scope of this work. Although the analysis of the residuals indicated potential heteroscedasticity in the data (Fig. S2a, S2b, Supplementary Material), the short duration of the overlapping time series justified applying a constant bias correction of + 2.67 µatm to pCO_{2atm_E2M3Ar}. To evaluate the robustness of this correction, a comparison between pCO_{2atm} derived from the CAMS reanalysis of the European Centre for Medium-Range Weather Forecasts (ECMWF; Agustí-Panareda et al., 2023), was also considered (Figure S3, Supplementary Material). The difference between monthly pCO_{2atm} data at Lampedusa (LMP) and at EMSO-E2M3A between 2003 and 2021 was 2 ppm which is similar to the offset estimated in the four-month period. Finally, wind speed (WSPD, m s^{-1}) was measured by a Young sensor on the meteorological station at EMSO-E2M3A (Cardin et al., 2025b; Dentico et al., 2025) with a manufacturer accuracy of ± 0.3 m s^{-1} and was used as input for CO_2 flux calculation. Given that at EMSO-E2M3A wind speed is measured at 2 m height and CO_2 air-sea flux calculation requires the standard reference height of 10 m (Wanninkhof, 2014), a conversion was performed using a logarithm wind speed profile according to:

$$u_{LOG(z)} = (ln(z/z_0) \,/\, ln(z_m/z_0))u_{(zm)} \quad (3)$$

where $u_{LOG(z)}$ is the wind speed (m s^{-1}) at the desidered height (10 m), z is the desidered measurement height (10 m), z_m the actual measurement height (2 m), z_0 is the roughness length that for oceanic regions was set equal to 1.52 x 10^{-4} (Peixoto and Ort, 1992) and $u_{(zm)}$ is the wind speed (m s^{-1}) measured at EMSO-E2M3A at 2 m height.

3.2. Model data

The EU Copernicus Marine Service (CMEMS) provides regular and systematic information on the ocean physics and biogeochemistry for the global ocean and the European regional seas (Le Treon et al. 2019). Data from different Mediterranean CMEMS products were used as an additional reference to investigate the variability of the in situ pCO_{2sw} and FCO_2. In particular, the following modelling products were used: the Sea Physics Reanalysis (PHY, Escudier et al., 2021) for the physical variables of surface temperature (SST, °C), salinity (Sal) and Mixed Layer Depth (MLD, m), the Biogeochemistry

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Reanalysis (RD; Cossarini et al., 2021) and the Biogeochemistry Analysis and Forecast product (AF; Salon et al., 2019) for pCO_{2sw} (µamt) and FCO_2 (mmol m^{-2} day^{-1}). Additionally, the Ocean Color Satellite product (Volpe et al., 2019) of the surface chlorophyll-a (Chl-a, µg l^{-1}) was used as a proxy of primary production. Detailed information on the models and variables used are summarized in Table 1. The time series presented here are spatial averages of the grid points in the 10 km radius from EMSO-E2M3A from the native spatial resolution of 4.5 km and 1 km for models and satellite data, respectively.

Table 1. Overview of the Copernicus Marine Service (CMEMS) products used in this work.

CMEMS product name	Variables used in this work	DOI	Reference
Mediterranean Sea Physics Reanalysis (PHY)	SST, Sal, MLD	https://doi.org/10.25423/CMCC/MEDSEA_MULTIYEAR_PHY_006_004	Escudier et al., (2021)
Mediterranean Sea Biogeochemistry Reanalysis (RD)	pCO_{2sw}, FCO_2	https://doi.org/10.25423/cmcc/medsea_multiyear_bgc_006_008_medbfm3	Cossarini et al., (2021)
Mediterranean Sea Biogeochemistry Analysis and Forecast (AF)	pCO_{2sw}, FCO_2	https://doi.org/10.25423/cmcc/medsea_analysisforecast_bgc_006_014_medbfm4	Salon et al., (2019)
Mediterranean Sea, Bio-Geo-Chemical, L4, monthly means, daily gapfree and climatology Satellite Observations (1997-ongoing)	Chl-a	https://doi.org/10.48670/moi-00300	Volpe et al., (2019)

ERA5 wind product, which is the fifth generation of ECMWF reanalysis for the global climate and weather (Hersbach et al., 2023), was also used and compared with EMSO-E2M3A wind measurements. ERA5 provides hourly estimates for a large number of atmospheric, ocean-wave and land-surface quantities from 1940 to present. The spatial resolution of atmospheric data is 0.25° x 0.25° and wind speed ($WSPD_{ERA5}$, m s^{-1}) in the subregion close to EMSO-E2M3A (30 km radius) was calculated according to the following:

$$WSPD_{ERA5} = \sqrt{u^2 + v^2} \quad (4)$$

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where u^2 is the square of the 10 m u-component (m s^{-1}), which is the eastward horizontal wind speed, while v^2 is the square of the 10 m v-component (m s^{-1}) that represents the northward horizontal wind speed. ERA5 wind speed data were selected for two main reasons: (i) wind reanalysis products, unlike in situ time series, provide continuous spatial and temporal coverage without observational gaps; (ii) ERA5 wind data are used as the wind forcing input in the Mediterranean Sea Physical and Biogeochemistry Reanalyses. Thus, considering that CO_2 air-sea flux in the CMEMS products and in the present work was computed following the same formulation (Wanninkhof, 2014), the use of the same wind dataset, allowed a focus on the analyses of pCO_{2sw} difference between in situ data and model outputs. Nevertheless, a validation of the ERA5 wind data using local wind conditions at EMSO-E2M3A and a discussion on the uncertainties introduced by the use of ERA5 data in computing FCO_2 will be presented.

3.3. Thermodynamic calculations

The direction and magnitude of FCO_2 is governed by the difference between pCO_{2sw} and pCO_{2atm} and the air-sea CO_2 gas transfer velocity (Takahashi et al., 2002):

$$FCO_2 = k_0 k (pCO_{2sw} - pCO_{2atm}) \quad (5)$$

where k_0 is the solubility coefficient of CO_2 at in situ temperature and salinity (Weiss, 1974; Zeebe and Wolf-Gladrow, 2001) and k is the gas transfer velocity (m day^{-1}). In this study, if the $FCO_2 < 0$ the flux is from air to seawater, on the contrary if $FCO_2 > 0$ the flux is from the seawater to the atmosphere. Several algorithms for k calculation exists, here the parametrization proposed by Wanninkhof (2014) was used:

$$k = 0.251 u^2 (Sc/660)^{-0.5} \quad (6)$$

where u is the 6-hourly wind speed averages (m s^{-1}) at 10 m height and Sc the Schmidt number for CO_2. Wanninkhof (2014), hereafter W14, has been proved to best represent the relationship between wind speed and gas exchange at a regional-to-global scale. For instance it was used in similar studies in the Mediterranean Sea (Pecci et al., 2024; Martellucci et al., 2025) and in the Adriatic basin (e.g., Urbini et al., 2020; Cantoni et al., 2024). Acknowledging that W14 provides the best fit with the Cross-Calibrated Multi-Platform (CMPP) wind product (Atlas et al., 2011), this formulation was applied using wind speed measurements from EMSO-E2M3A and from ERA5. This choice ensures methodological consistency in the comparison between CO_2 flux calculated from in situ data and those from the models.

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3.4. Thermal and non thermal component of pCO_{2sw}

Thermal (pCO_{2sw_T}, µatm) and non-thermal (pCO_{2sw_NT}, µatm) components of pCO_{2sw} were estimated according to Takahashi et al. (2002). The thermal component is associated to the effect of temperature on pCO_{2sw}, while the non-thermal component can be attributed to other factors not strictly related to temperature, as biological activity (photosynthesis and respiration), changes in dissolved inorganic carbon (DIC), mixing or advective processes and gas exchange with the atmosphere. pCO_{2sw_T} and pCO_{2sw_NT} have been computed using the following equations:

$$pCO_{2sw\_T} = mean(pCO2_{sw})^{0.0423(SST_{obs} - SST_{mean})} \quad (7)$$

$$pCO_{2sw\_NT} = pCO2_{sw}^{0.0423(SST_{mean} - SST_{obs})} \quad (8)$$

where, *mean* refers to yearly mean values of sea surface temperature (SST, °C), while the other variables (pCO_{2sw} and SST_{obs}) refers to the daily values measured during the study period.

4. Results and Discussion

4.1. pCO_2 dynamics and hydrography in the SAP

The time series of the daily surface pCO_{2sw} between 2015 and 2024 is presented in Fig. 2a. The incomplete coverage of the full seasonal cycle in several years, prevented a detailed assessment of interannual variability. Therefore, the discussion presented in this section mainly focuses on the seasonal patterns and its main drivers, and, when possible, on interannual differences of the seasonal cycle.

Mean winter values were around 380 µatm and mean summer values reached around 484 µatm, resulting in a seasonal amplitude of about 100 µatm. During winter, low sea surface temperature (SST < 15 °C; Fig. 2b) increases CO_2 solubility, leading to lower pCO_{2sw}. However, during winter convection, vertical mixing increased surface pCO_{2sw}, as shown by the pCO_{2_NT} component (Fig. 2a). These increases were particularly evident between late December and late February of 2016–2017, 2017–2018, 2020–2021, and 2023–2024 (Fig. 2a). As described in Touratier et al. (2016) and in Ingrosso et al. (2017), vertical convection brings intermediate/deep CO_2-rich waters to the surface, causing increases in surface pCO_{2sw}. Positive AOU values during these periods (Fig. 2c) confirmed the occurance of vertical mixing and the upward displacement of oxygen-depleted intermediate waters as described also in Martellucci et al. (2024b). The post-convection periods (usually from March to May-June) were characterised by a phytoplankton bloom (Fig. 2e), but its direct effect on pCO_{2sw} was less clear as few data were available in these periods. However, photosynthesis during the bloom, as suggested by negative AOU values and an increase in oxygen concentrations at the surface (Fig. 2c), could likely contribute to decreasing pCO_{2sw}. In spring, surface warming began, leading, in summer, to

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maximum SST values (> 25 °C) and strong stratification. During this period, pCO_{2sw} reached its annual maximum, closely following the pCO_{2sw_T} component and indicating a strong thermal effect (Fig. 2a). Independent measurements from an Unmanned Surface Vehicle (USV) operating in the area in July 2019 during the ATL2MED experiment (Martellucci et al., 2025) further confirmed this pattern, showing coherent short-term variations with the EMSO-E2M3A time series. Interestingly, higher pCO_{2sw} values were recorded in summer 2022, with a peak in July 2022, coinciding with the occurrence of a Mediterranean Marine Heatwave (MHW). In the SAP, Pirro et al. (2024) detected positive temperature anomalies across the whole water column, with the strongest warming at the surface. Thus, the elevated pCO_{2sw} observed in this period might be linked to the MHW, although further analyses, for instance in relation to wind change patterns (e.g., Pecci et al., 2024) would be required to confirm this hypothesis. The annual cycle of surface pCO_{2sw} in the SAd was comparable to other regions of the Mediterranean Sea with generally lower values than those observed in the SAd (Dentico et al., 2025). Similar seasonal variations especially in winter were described for the northern Adriatic shelf (Ingrosso et al., 2016; Urbini et al., 2020; Cantoni et al., 2024), where intense Bora wind events and vertical mixing periodically disrupt water column stratification, promoting an efficient exchange between bottom and surface pCO_{2sw}. However, unlike the SAd, the riverine inputs in this area also play a key role in modulating the carbonate system dynamics (e.g., Giani et al., 2023). In the convective region of the northwestern Mediterranean Sea, several studies have emphasized the importance of vertical mixing, horizontal advection and biological productivity in driving pCO_{2sw} variability (e.g., Merlivat et al., 2018; Fourrier et al., 2022; Ulses et al., 2023). In the SAd the effect of biological activity was less clear because of data gaps. Nevertheless, further investigations could be essential to clarify the role of biological processes in shaping the local carbon cycle as highlighted in previous studies (Socal et al., 2012; Cerino et al., 2012). Finally, in non-convective regions such as the eastern Mediterranean Sea (Frangoulis et al., 2024), or the Lampedusa site (Pecci et al., 2024), other processes appear to control pCO_{2sw} variability.

The analysis of hydrological data showed the highly dynamic characteristics of the region. First, the intensity and occurrence of convection in the SAd has varied substantially among years (Fig. 2d). Weaker events were recorded in 2015, 2016, 2019, and 2020, whereas deeper mixing (> 600 m) occurred in more recent years (especially after 2022). These interannual variability resulted from strong/weak air-sea interactions, where stronger heat losses could occur especially under the influence of the cold and dry Bora wind (Le Meur et al., 2025). Variations in the regional hydrographic structure, particularly changes in salinity (Amorim et al., 2024; Le Meur et al., 2025), also affected the stability of the water column and the depth of convection. This variability in salinity was associated with the inflow of Levantine/Ionian surface water, which is regulated by changes in the Northern Ionian Gyre (NIG) vorticity (Gačić et al., 2010; Rubino et al., 2020; Menna et al., 2022; Civitarese et al., 2023). The influence of NIG in the SAd was evident in the salinity measurements (Fig. 2f), which showed periods of higher salinity (> 39 in 2017, 2021, 2022) and lower salinity (< 38.5 in 2015, 2018).

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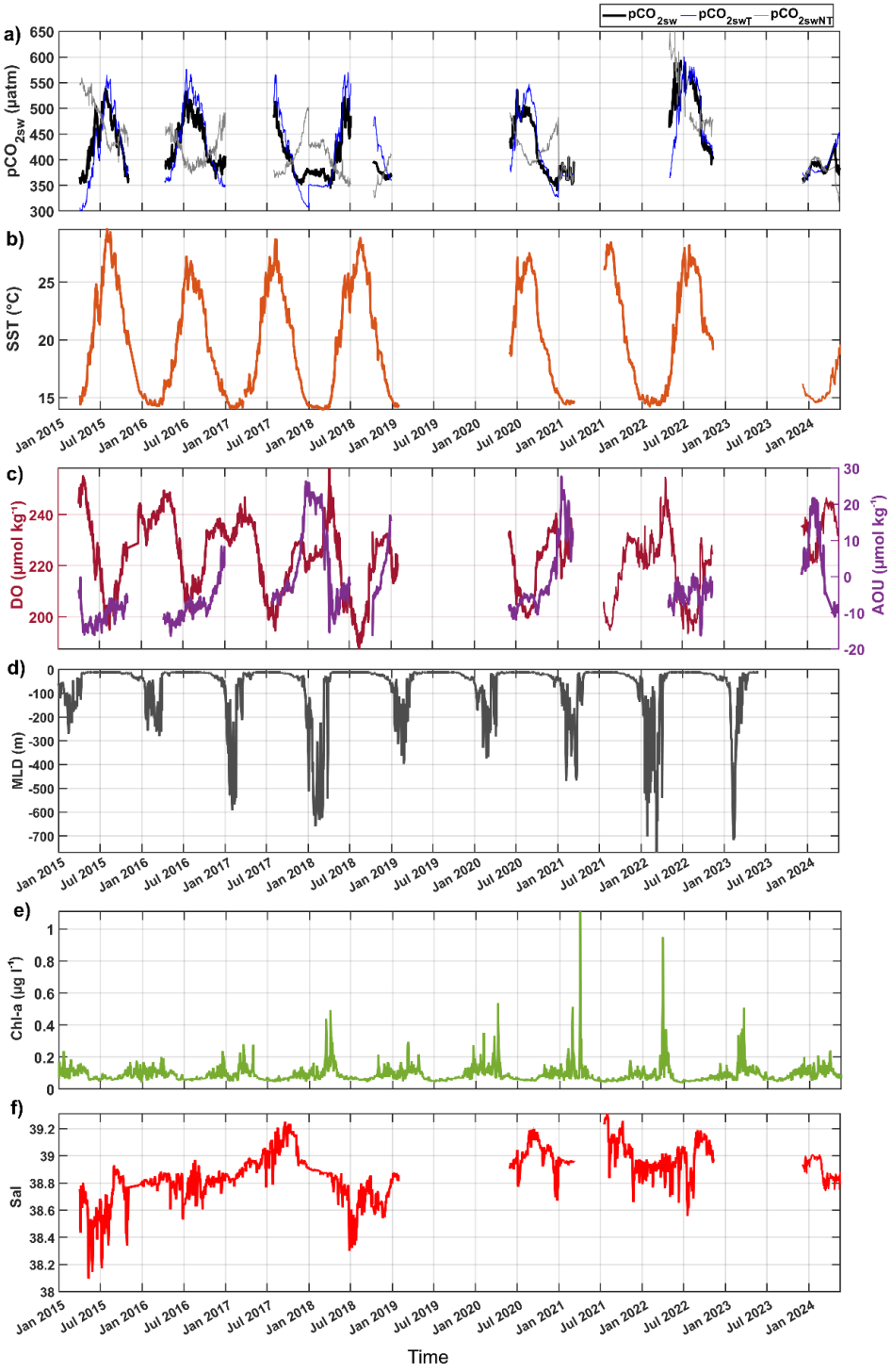

357

358 **Figure 2.** Time series of daily a) Partial pressure of CO_2 in seawater (pCO_{2sw}, µatm) and the thermal (pCO_{2_T}, µatm) and non

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thermal (pCO_{2_NT}, µatm) components of pCO_{2sw} (µatm) in black, blue and grey, respectively; b) Sea surface temperature (SST, °C); c) Dissolved oxygen (DO, µmol kg^{-1}) and Apparent Oxygen Utilization (AOU, µmol kg^{-1}) derived from DO measured by the SBE37 ODO sensor in dark red and violet respectively; d) Mixed Layer Depth (MLD, m) from the CMEMS Mediterranean Sea Physics Reanalysis; e) Chlorophyll-a (Chl-a, µg l^{-1}) used here as a proxy of primary production from the CMEMS Mediterranean Sea, Bio-Geo-Chemical, L4, monthly means, daily gapfree and climatology Satellite Observations (1997-ongoing); and f) Sea surface salinity (Sal). Time series (a, b, c and f) refers to the data measured by several instruments deployed at 2 m depth at EMSO-E2M3A between April 2015 and May 2024. Data gaps in the series were mostly due to maintenance operations and/or discarded data because they failed the quality-control procedures described in Dentico et al. (2025). Modified from Dentico et al. (2025).

4.2. CO_2 flux: source-sink dynamics

Daily FCO_2 in the SAd presented in this section has been computed according to Eq. (5) and Eq. (6) using as input pCO_{2sw}, pCO_{2atm_E2M3Ar} (Sect. 3.1) and 6-hours averaged wind speed data from EMSO-E2M3A corrected at 10 m height (Sect. 3.3). CO_2 air-sea flux in the SAd presents two dominant phases: a source period, generally associated with post-convection/summer months (positive values in Fig. 3a), and a sink period, typically occurring during winter and during episodes of winter convection (negative values in Fig. 3a). While the intensity of daily values during sink and source phases exhibited high interannual variability, the timing of the transition months, i.e., the periods when the SAd shifts from a source (May) to a sink (October), occurred regularly (Fig. 3b).

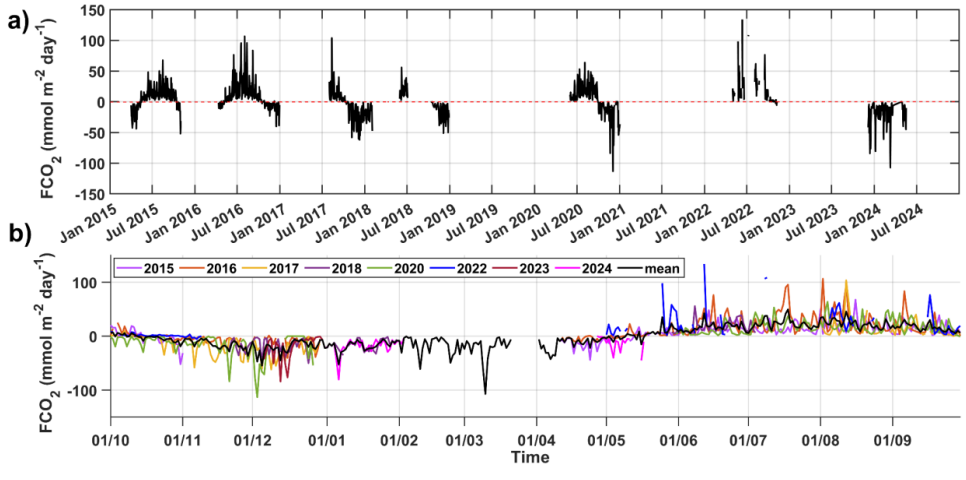

Figure 3. a) Time series of daily CO_2 flux (FCO_2, mmol m^{-2} day^{-1}) calculated with in situ measurements in the period 2015-2024 at EMSO-E2M3A; b) Daily averages of CO_2 flux calculated in the different years (coloured lines) and the mean daily FCO_2 (mmol m^{-2} day^{-1}) over the entire period (2015-2024; black line). Negative flux represents CO_2 influx from the air to the sea and positive flux represents CO_2 outgassing from the sea to the air.

Given the observed variability (i.e., high daily variability with a regular annual cycle) and the presence of substantial data gaps in the FCO_2 time series, two complementary computational approaches were

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applied to derive robust estimates of mean CO_2 fluxes in the SAP over the past decade. By considering two different orders in the process of aggregating data for computing averages, the sensitivity of data sampling irregularity to the overall mean was verified. In the first approach (hereafter M1), the daily means for each day of the year were calculated. Outliners were then identified and removed through visual inspection, with particular attention to values not supported by a sufficiently large number of observations. Finally, monthly means were derived, and the overall mean for the entire study period (2015-2024) was computed from the 12 monthly averages. In the second approach (hereafter M2), a 2015-2024 time series of the monthly values is computed for those months with at least 14 valid daily values. The mean over the full period was subsequently obtained from these monthly values. A summary of the monthly means obtained with M1 and M2 is reported in Table 2.

Table 2. Monthly mean of FCO_2 (mmol m^{-2} day^{-1}) in the SAd calculated with in situ data from the EMSO-E2M3A regional facility in the period 2015-2024 using two different computation methods. Relative difference was calculated as M1 - M2 divided by M1.

Month of the year	M1 (mmol m^{-2} day^{-1})	M2 (mmol m^{-2} day^{-1})	M1 - M2	Relative difference
January	-17.92	-17.89	-0.04	0.0020
February	-16.75	-15.96	-0.78	0.0469
March	-12.79	-12.79	0.00	0.0000
April	-14.26	-11.02	-3.23	0.2269
May	6.36	9.80	-3.44	-0.5410
June	16.67	16.31	0.36	0.0215
July	22.49	21.06	1.43	0.0635
August	24.11	22.90	1.22	0.0504
September	15.61	15.58	0.03	0.0017
October	-1.99	-1.88	-0.11	0.0577
November	-15.30	-15.62	0.32	-0.0209
December	-20.14	-19.69	-0.45	0.0222

Both methods produced consistent results, with an average difference of approximately 5 % between M1 and M2. The largest discrepancies between the two methods occurred in April and May. In April these can be due to the lower data availability (Fig. 3b), as only two years of data were available. On the contrary, in May a transition between source and sink conditions occurs, thus explaining the larger differences between M1 and M2. Similarly, in February, data for only one year (2024) was available throughout the month with the addition of a few days at the beginning of February 2018 making this

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approach not robust enough to have reliable results (higher difference between M1 and M2). Finally, in March data were available only in 2024, and the proposed aggregating processes produced no difference between M1 and M2. Notwithstanding these potential limitations derived by data availability, the results indicated that, over the last decade, the SAd has functioned predominantly as a moderate carbon sink. For the period 2015-2024, mean FCO_2 values ranged from -1.15 mmol m^{-2} day^{-1} (M1) to -0.76 mmol m^{-2} day^{-1} (M2). Although modest in magnitude, these values consistently pointed to a net CO_2 uptake, underscoring the potential role of the SAd in regional carbon sequestration, as suggested by Ingrosso et al. (2017). Further, these results confirm the role of dense water formation sites as primary drivers of carbon sequestration. Indeed, the northern Adriatic Sea has been reported to act as an effective CO_2 sink during winter, spring, and autumn, with mean daily fluxes of about -2.9 mmol m^{-2} day^{-1} (Catalano et al., 2014; Cantoni et al., 2024). In the Gulf of Lion, Ulses et al. (2023) showed that the area functions as a net CO_2 sink on an annual scale, with an estimated carbon sequestration rate of approximately -1.29 mmol m^{-2} day^{-1} (estimated mean was -0.47 mol C m^{-2} $year^{-1}$).

4.3 Estimated uncertainties in FCO_2

The accuracy of the CO_2 flux estimates presented in this study was influenced by several systematic sources of uncertainty, arising from the type of data used to compute the two relevant parts of the W14 formula, i.e., the the gas transfer velocity k and the difference between pCO_{2sw} and pCO_{2atm} (ΔCO_2). To assess the source of uncertainty related to k, three different wind datasets were used to compute CO_2 flux other than the one used in Sec. 4.2. These considerations are particularly relevant given the presence of temporal gaps in the time series presented here. The first case (hereafter U1) considered the conversion applied to EMSO-E2M3A wind speed data from 2 m to 10 m height (see Sec. 3.3). The second case (hereafter U2) accounted for the effect of a different temporal resolution considering a daily average of the wind data directly calculated from hourly observation without performing 6-hourly means. The use of 6-hourly wind speed averages is widely adopted as it smooths extreme values, reduces noise in buoy data, better represents the slow air–sea CO_2 exchange, and ensures consistency with model outputs. The third case (hereafter U3) used wind data from ERA5. Considering U3 is particularly relevant especially when in situ measurements are unavailable, and model-derived data must be integrated. Moreover, given that RD uses the same W14 formula and ERA5 wind data, the assessment of U3 can be used to help disentangling model errors that derive from the air-sea flux calculation (e.g., different wind products) from those derived from the ΔCO_2 discrepancies. Uncertainty in each of the three cases was quantified as the mean difference between fluxes calculated using the reference condition (10 m in situ wind speed averaged every 6 hours) and the alternative inputs (2 m height and 6 hours average in situ wind speed, for U1; daily average of 10 m height in situ wind speed, for U2; and 10 m height and 6 hours average ERA5 wind speed, for U3). For the ΔCO_2, the systematic uncertainty associated with the use of pCO_{2atm} derived using xCO_2 from Lampedusa site (Sec. 3.1) was considered. This latter, hereafter referred to as U4, was estimated by comparing winter fluxes calculated

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with the uncorrected pCO_{2atm} to those calculated after adding +2.67 µatm to the pCO_{2atm} time series (Sec. 3.1). All the uncertainties, except U4, were computed separately for two extended seasonal regimes: the summer/source period (from April to September) and the winter/sink period (from October to March). U4 was restricted to the winter period only as the offset of +2.67 µatm was computed considering winter months only (December to March, Sec. 3.1). A summary of the results is shown in Fig. 4.

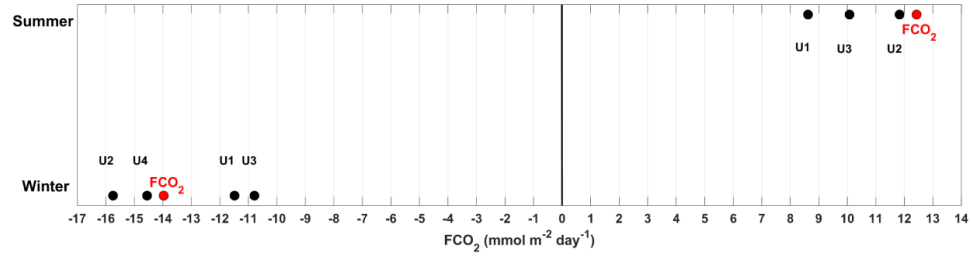

Figure 4. Summary of the different sources of uncertainties (U1, U2, U3, U4) considered in the study associated with the estimated FCO_2 (mmol m^{-2} day^{-1}) in the SAd (FCO_2 in red) in the period 2015-2024 calculated as described in Sec. 4.2. Winter includes the months from October to March and summer includes the months from April to September.

The different sources of uncertainty influenced FCO_2 estimates in different ways across seasons. The largest seasonal differences were observed for U1 and U3, whereas U2 showed lower variability between winter and summer. Among the three, U2 contributed the least to the overall uncertainty especially during summer, suggesting that the choice between using daily mean calculated from 6-hourly means or daily average calculated from hourly observations (without performing 6-hourly means) wind speed had only a minor effect on the final FCO_2 estimates. However, this choice appeared to have a higher influence during winter. The effect of using wind speed data at a lower height than the standard 10 m height (U1), as proposed in W14, has already been discussed (e.g., Griessbaum et al., 2010; Nickford et al., 2022; Nickford et al., 2024). The authors have shown that wind speed measured closer to the air–sea exchange interface could better represent the local forcing, particularly under conditions of high atmospheric stratification. Such measurements may also capture transient phenomena, including gusts and micro-turbulence, and could improve our understanding of the role of wave breaking and bubble-mediated transfer in modulating the CO_2 flux. While these aspects are beyond the scope of the present study, they highlighted the value of further investigations into near-surface wind dynamics for the estimation of FCO_2. U3 showed the largest differences with respect to FCO_2 estimated as described in Sec. 4.2, underscoring potential limitations in using ERA5 reanalysis data as a reliable regional proxy for local wind speed conditions. A more detailed analysis (Fig. S4, S5, Supplementary Material) revealed high differences between the wind speed measured at EMSO-E2M3A and ERA5 especially in high Beaufort scale wind (https://www.rmets.org/metmatters/beaufort-

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476 wind-scale). Given the quadratic dependence of k on wind speed, as a result, the choice of the wind
477 speed field used is expected to lead to changes in FCO_2 as emphasized by Takahashi et al. (2002).
478 Considering the uncertainty of the ΔCO_2 components, errors associated with corrected or not corrected
479 pCO_{2atm} in the SAd were negligible. Finally, it is important to mention that in respect to ΔCO_2 the error
480 related to the use of in situ sensor-based pCO_{2sw} as input for FCO_2 should also be computed. Sensor-
481 based pCO_{2sw} not always met the manufacturer and the ICOS or SOCAT accuracies (Steinhoff et al.,
482 2025). As shown in Dentico et al., (2025) the measured values by Pro-Oceanus membrane sensor can
483 report higher (>10 µatm) differences with pCO_{2sw} calculated from discrete seawater samples. Here, it
484 was not possible to compute a statistically robust measure of this uncertainty. This was due to the very
485 low number of discrete seawater samples and the bias of their temporal distribution (Dentico et al.,
486 2025). Most of the available pCO_{2sw} from discrete seawater samples were collected in October and not
487 only failed to adequately represent the full seasonal cycle of CO_2. Additionally, October was the month
488 that showed the transition from the positive to negative phases possibly emphasizing differences in
489 FCO_2 calculation. While the random component of uncertainty can be quantified for pCO_{2sw} (e.g., using
490 standard bootstrapping approaches based on the manufacturer-specified precision of the pCO_{2sw} sensor),
491 the focus here was on the potentially systematic sources of uncertainty in the computation of FCO_2.
492 This choice reflected the substantial effort involved in assembling multiple source dataset.
493
494 **4.4. pCO_{2sw} and FCO_2: in situ data and model comparison**
495 The in situ pCO_{2sw} and physical data proved to be a reliable asset for model validation, thus a
496 comparison between the RD and AF CMEMS products for pCO_{2sw} and FCO_2 was computed. The
497 comparison between daily pCO_{2sw} from CMEMS (Sect. 2) and pCO_{2sw} measured by the probe for a
498 decade-long period highlighted a coherent temporal evolution (Fig. 5). A RMSE of 35.96 µatm and a
499 significant correlation coefficient of 0.82 (p *value* < 0.01) between the two datasets was found.
500 Nevertheless, during summer, model data were on average higher than pCO_{2sw} from the probe, with a
501 mean difference between RD and the probe data of +34.22 µatm. The only exception was in 2022, when
502 pCO_{2sw} from the probe was higher than CMEMS data (both RD and AF). On the contrary, in winter RD
503 data were on average lower than the probe, with a mean difference between the two datasets of -26.87
504 µatm. This can be explained by the increase in the pCO_{2sw} shown by probe data between late December
505 and late February that was not resolved by the model, which underestimated it by approximately 45
506 µatm. Finally, in autumn and spring the mean differences were smaller (+5.13 µatm and -16.12 µatm,
507 respectively). By contrast, with lower intensity, the AF product was able to capture this increase (Fig.
508 5). Similarly to RD, also AF was not able to consistently reproduce the higher pCO_{2sw} values measured
509 by the probe in summer 2022.
510

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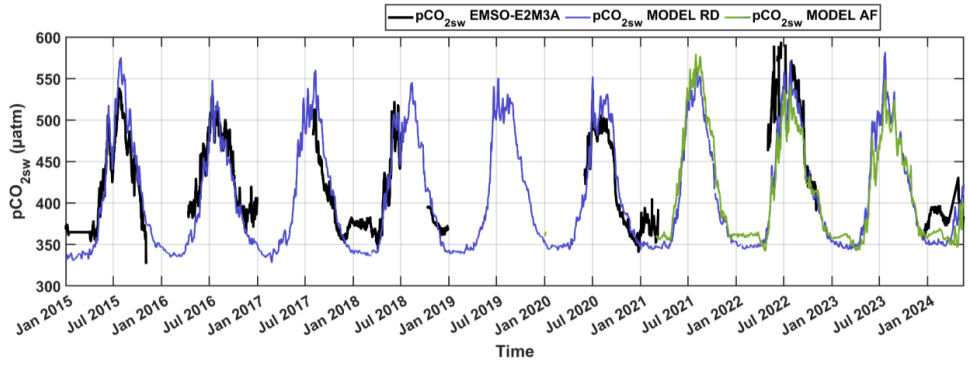

Figure 5. Time series of daily pCO_{2sw} (µatm) measured at the EMSO-E2M3A regional observatory in black, pCO_{2sw} (µatm) from the Mediterranean Sea Biogeochemistry Reanalysis (RD) in blue and the Mediterranean Sea Biogeochemistry Analysis and Forecast (AF) in green. RD data after July 2022 were integrated with the interim reanalysis.

The comparison between FCO_2 derived from in situ data and from the model is presented in Fig. 6. Both datasets consistently capture the two main seasonal phases of the region, with a source period during summer and a sink period during winter. However, notable differences in absolute values emerged, particularly in summer. A main factor in these differences was related to the pCO_{2sw} measurements as discussed in the previous section. Additionally, in both seasons, the different wind forcing used by the model (ERA5) could also be a contributing factor of the FCO_2 difference (see Sect. 4.3 and Fig. S5, Supplementary Material). On the contrary, the difference between model and in situ temperature and/or salinity was not considered a driving factor of the in situ and RD FCO_2 difference (Fig. S6, Supplementary Material). Nevertheless, an RMSE of 16.89 mmol m^{-2} day^{-1} with a correlation coefficient of 0.89 (p *value* < 0.01) was calculated between FCO_2 from RD and FCO_2 derived from observational data.

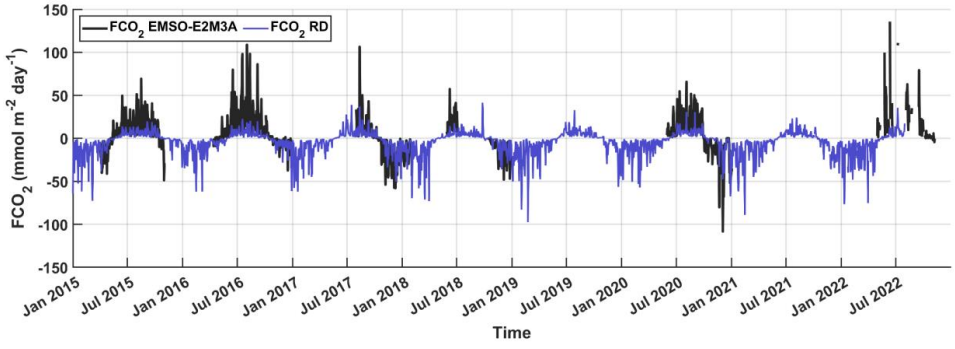

Figure 6. Time series of daily FCO_2 (mmol m^{-2} day^{-1}) calculated with in situ data measured at the EMSO-E2M3A and FCO_2 (mmol m^{-2} day^{-1}) from the Mediterranean Sea Biogeochemistry Reanalysis (RD) represented by the black and violet curves respectively. Model data after July 2022 were integrated with the interim reanalysis.

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Considering the relatively good performance of the RD, and the temporal bias in the in situ FCO_2 time series (e.g., the winter periods were by far undersampled with respect to summer periods), the use of the CMEMS RD product to compute the overall FCO_2 average filling the gaps of the in situ data was tested. A bias (B) of the CMEMS RD was calculated as the difference between the mean flux over the entire period (2015-2024) and the mean flux considering only the days with observations. B was then added to the mean flux calculated with in situ observations, resulting in -4.9 mmol m^{-2} day^{-1} and -4.5 mmol m^{-2} day^{-1}, respectively for the two M1 and M2 methods. Even if these estimations should be considered with caution, they further confirm that the southern Adriatic acted as a moderate carbon sink over the last decade.

5. Conclusion

A time series of pCO_{2sw} and hydrography from autonomous sensors over the past 10 years were analyzed to characterize pCO_{2sw} and carbon flux in the dense water formation site of the southern Adriatic Sea. The data were collected by several sensors deployed at the EMSO-E2M3A South Adriatic regional facility and ICOS ERIC observatory (nominal position 41.5053°N, 18.0806°E) which is located in the central and deepest part of the SAd, the SAP. Surface pCO_{2sw} dynamics were characterized by strong seasonal fluctuations, with a difference of 100 µatm between winter and summer. In winter, average pCO_{2sw} were around 380 µatm, with marked increase especially during wintertime convection periods when CO_2-rich intermediate and deep water were upwelled to the surface. In summer, average values increased up to around 500 µatm driven by higher sea surface temperatures. The effect of biological processes was difficult to identify due to lower availability of data during post-convection/bloom periods. CO_2 fluxes were characterized by two distinct regimes of post-convection/summer CO_2 released to the atmosphere (mean summer month/source flux of +12.43 mmol m^{-2} day^{-1}) and convection/winter CO_2 ocean uptake (mean winter months/sink flux of -15.82 mmol m^{-2} day^{-1}). One of the key results of this study was to demonstrate that over the past decade the SAd acted as a moderate carbon sink. Two different orders of aggregating the data for computing decadal averages were used due to the sampling irregularity. These calculations resulted in a mean sink flux of -1.15 mmol m^{-2} day^{-1} (M1) and -0.76 mmol m^{-2} day^{-1} (M2) in the period 2015-2024. Several sources of systematic uncertainty associated with the two most relevant parts of the flux formula, i.e., the gas transfer velocity (k) and ΔCO_2, were also quantified. For k, the selection of the wind forcing to be used in FCO_2 calculation is one of the primary sources of uncertainties. Particularly, the correction applied to convert in situ wind speed data from 2 m height to 10 m height and the use of ERA5 dataset as input variable for the calculation of FCO_2. Thus, careful consideration must be given to both the wind product selected and the height at which wind is measured or modeled, particularly in coastal areas or under high-wind conditions where gas exchange may be over- or underestimated (Nickford et al., 2024).

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Furthermore, as many oceanic areas lack in situ wind observations, model-derived wind products (e.g., ERA5, CCMP) are frequently used. Assessing the reliability and limitations of these datasets is therefore critical for improving flux estimates in data-sparse regions. Regarding ΔCO_2, the use of pCO_{2atm} from another location appeared to have a minor influence on the final FCO_2. While in this study the focus was on systematic uncertainty, the pCO_{2sw} one was not estimated due to the lack of discrete seawater samples. By proving to be an important asset for model validation, the pCO_{2sw} and hydrographic time series allowed to quantify existing specific discrepancies in the regional CMEMS model product such as a lack in winter pCO_{2sw} increase, and over/underestimation of the seasonal amplitude. Nevertheless, the integration of model and observational data further confirms that the SAd was a site of moderate atmospheric CO_2 sink in the last decade.

The SAd, as many other regions in the Mediterranean Sea, is currently undergoing profound physical changes, including increasing sea surface temperature, rising salinity, and the potential intensification of extreme events. These trends are likely to affect convection intensity and timing, with potential consequences for carbon dynamics in the basin on a climatic scale. In this context, the long-term monitoring carried out in the region, by combining sustained in situ observations with modeling approaches, are necessary to fully understand the complex interplay between physical forcing, biogeochemical processes, and carbon dynamics in the context of climate change.

Data availability

The in situ data used in this study are freely accessible at the National Oceanographic Data Center (NODC) of the National Institute of Oceanography and Applied Geophysics (https://doi.org/10.13120/y2hw-1j63; Cardin et al., 2025). Model data are also publicly available through the Copernicus Marine Service website following the links provided in the manuscript.

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Author contribution:

CD: data curation, investigation, validation, writing (original draft), writing (review and editing), conceptualisation, formal analysis. GCos: investigation, writing (review and editing), conceptualisation. GCiv: investigation, writing (review and editing), conceptualisation. MG:investigation, writing (review and editing), conceptualisation. AR: investigation, writing (review and editing), conceptualisation. VC: funding acquisition, project administration, investigation, writing (review and editing), conceptualisation, supervision.

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Competing interest:

The authors declare that they have no conflict of interest.

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