CO_2 and hydrography acquired by Autonomous Surface Vehicles from the Atlantic Ocean to the Mediterranean Sea: data correction and validation

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Abstract. The ATL2MED demonstration experiment involved two autonomous surface vehicles from Saildrone Inc. (SD) which travelled a route from the eastern tropical North Atlantic to the Adriatic Sea between October 2019 and July 2020. This nine-month experiment in a transition zone between the temperate and tropical belts represents a major challenge for SD's operations. The sensors on board were exposed to varying degrees of degradation and biofouling depending on the geographical area and season, which led to a deterioration of the measurements. As a result, some maintenance measures were required during the mission.

We address the difficulty of correcting the data during a period of COVID-19 restrictions, which significantly reduced the number of discrete samples planned for SD salinity and dissolved oxygen validation. This article details alternative correction methods for salinity and dissolved oxygen. Due to the lack of *in situ* data, model products have been used to correct the salinity data acquired by the SDs, and then the resulting corrected salinity was validated with data from fixed ocean stations, gliders, and Argo floats. In addition, dissolved oxygen data acquired from SDs after correction using air oxygen measurements were tested and found to be coherent with the variation of oxygen concentrations expected from change in temperature and phytoplankton abundance (from chlorophyll-a). The correction methods are relevant and useful in situations where validation capabilities are lacking, which was the case during the ATL2MED demonstration experiment. For future experiments, a more frequent sample collection would improve the data qualification and validation.

1 Introduction

Automated observations contribute to a steadily increasing knowledge of the ocean and its role in the global climate system. For a long time, fixed ocean stations and research vessels formed the backbone of the monitoring network. In recent years, efforts have been made to improve the frequency of acquisition through technological developments (*e.g.*, EU infrastructures ICOS, https://www.icos-cp.eu/; EMSO, https://emso.eu; EuroArgo,

https://www.euro-argo.eu). Among other improvements, fixed ocean stations and ships of opportunity (Lüger et al., 2004) were equipped with autonomous and accurate sensors for partial pressure of CO_2 (pCO_2) measurements in addition to sensors for complementary measurements (*e.g.*, water temperature, salinity, dissolved oxygen, pH, nutrients, fluorescence) needed to understand the dynamics and the effects of CO_2 fluxes on the carbon budget. Despite efforts to do so, it remains difficult to obtain a comprehensive overview of CO_2 fluxes at regional and larger scales because of very sparse coverage by fixed observatories, low measurement frequency and limited systematic reference measurements.

One way to address such observational gaps (Tanhua et al., 2019) is to develop and deploy Autonomous Surface Vehicles (ASV) equipped with a suite of sensors, and capable of measuring CO_2 fluxes at the air-sea interface with gas reference, high sampling frequency and real-time data transmission. ASV monitoring systems have the potential to collect data from large ocean areas and at a frequency that resolves processes at multiple time scales. Nevertheless, there are challenges with those surface monitoring systems, and one of the most important is the biofouling, which can interfere with measurements of *e.g.*, conductivity, dissolved oxygen and especially chlorophyll-a (Chl-a), and could ultimately render the sensors inoperable (*e.g.*, Delauney et al., 2010). Regular maintenance counteracts biofouling or at least reduces the impact on measurements, but this is not always possible due to long distance from shore or from the maintenance vessel. Therefore, the value of ASV data depends heavily on quality control and quality assurance.

During the 9-month-long demonstration experiment ATL2MED, two wind-driven Saildrone ASV (SD; Gentemann et al., 2020) manufactured by Saildrone Inc. (Alameda, CA, USA) were used to improve data coverage and link CO_2 surface observations at fixed ocean stations on a larger scale from the eastern tropical North Atlantic (ETNA) to the central Mediterranean Sea. SDs are prone to errors primarily due to sensor drift, which can be caused by either biofouling or malfunctioning sensor parts. During the ATL2MED demonstration experiment, problems were found with the data collected by several SD sensors, and severe biofouling occurred, as expected in such a long-duration experiment.

Still, the use of SDs provided the opportunity to expand and link fixed CO_2 observations at the surface on a larger scale, particularly during the COVID-19 pandemic when access to ocean platforms and ship visits were restricted or even prohibited. Furthermore, the demonstration experiment allowed us to focus SD measurements on different marine environments, the Atlantic Ocean and the Mediterranean Sea, which made it possible to assess the quality of measurements across a wide range of values. The experiment additionally evaluated the ability of such ASV to provide data with sufficient quality to be relevant for the scientific community.

The objective of the present work is to evaluate and correct the data collected by the SDs in order to provide a homogenised and comparable data set useful for the study of processes such as air-sea gas exchange in the Atlantic Ocean and Mediterranean Sea. While this paper focuses on the methods, a follow up paper will focus on biogeochemical processes occurring in the area.

2 Material

2.1 Data collection and experiment

The ATL2MED demonstration experiment took place between 18 October 2019 and 17 July 2020 as a joint effort among a number of European academic institutions and SD piloting team. A detailed description of the ATL2MED demonstration experiment can be found in Skjelvan et al. (2021). During the experiment, the SDs crossed the ETNA region, the Strait of Gibraltar, and the northern part of the western and central Mediterranean Sea including the Ligurian Sea, the Strait of Sicily, the Strait of Otranto, and the Adriatic Sea (Fig. 1).

The aim of the ATL2MED demonstration experiment was to (1) study eddies in the Canary Current upwelling system off West Africa jointly with a vessel-based research expedition (RV Meteor M160) and (2) to validate the CO_2 measurements acquired at 5 fixed ocean stations (DYFAMED, W1M3A, E2M3A, PALOMA, and MIRAMARE). This monitoring experiment was achieved with sensors and instruments installed on the SDs, but also equipment deployed at a number of facilities that were used to correct data from the SDs (see Section 3). Table 1 provides an overview of the various facilities and the times at which the SD visits were carried out. A detailed description of the instruments and sensors installed on the different platforms as well as their characteristics can be found in Tables S1, S2 and S3 of the Supplementary Material.

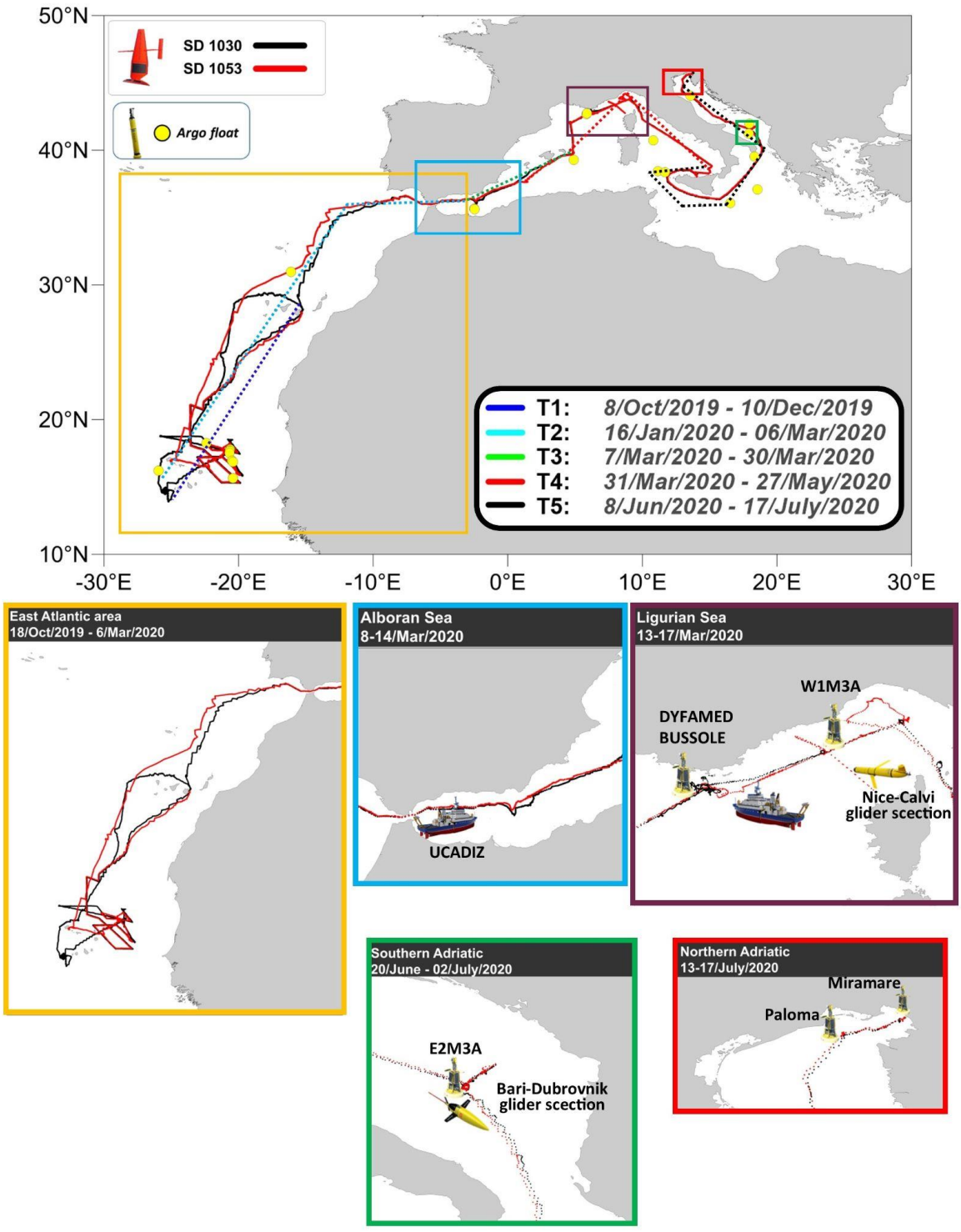

Figure 1. Study area, with the upper map showing the route of the two SDs (SD 1030 black and SD 1053 red lines), the positions of the Argo floats (yellow dots) and the SD routes divided into transects (T). The lower maps zoom in on areas with in-situ observations (buoys, ships and glider sketches).

Maintenance operations ensured the reliability and accuracy of the data collected by the SDs. Throughout the expedition, the data collected by the SDs were categorised into different transects, designated as T1, T2, T3, T4,

and T5. These transects corresponded to specific sections of the expedition timeline in terms of maintenance events (see Table S1 in Supplementary Material), which facilitates data correction.

The SDs were equipped with a number of autonomous sensors (CTD: conductivity, temperature, depth; dissolved oxygen; fluorescence; pH; pCO_2; meteorological sensors). This study focuses primarily on sensors acquiring temperature, salinity, dissolved oxygen, and pCO_2 data. This selection is based on the available options for correcting the SD datasets: some of the sensors (*e.g.*, fluorescence) were so severely affected by biofouling that it could not be accounted for, while others only worked for a short period of time (*e.g.*, Durafet Honeywell pH sensor). One of the SDs (SD 1030) was equipped with an ASVCO2 system developed by PMEL (NOAA's Pacific Marine Environmental Laboratory). The ASVCO2 system is a compressed version of the more voluminous system described in detail in Sutton et al. (2014). Water from a depth of approximately 0.5 m is fed into a bubble equilibrator (Friederich et al., 1995) and the partially dried xCO_2 is measured with an infrared detector (LI-COR 820 CO2 gas analyser). A two points calibration was used where the first is a reference gas from NOAA/ERSL, while the second is air purged for CO_2. An air inlet was mounted approximately 1 m above sea level and atmospheric xCO_2 was measured between measurements of the sea surface. See Table S2 in the Supplementary Material for the measurement frequency and initial accuracy of the SD sensors during the ATL2MED experiment.

2.2 Comparative datasets

2.2.1 Liguro-Provencal basin facilities

In the French EEZ, the open fixed station DYFAMED is located in the Ligurian Sea in the northwestern Mediterranean Sea. The CNRS (French National Centre for Scientific Research) is in charge of the station as part of the national MOOSE program (Coppola et al., 2019). At the DYFAMED site, a CARIOCA pCO_2 sensor ensures autonomous measurements and detailed description can be found in Merlivat et al. (2018). In addition, gliders are regularly operating the Nice-Calvi section where the DYFAMED site is located (MOOSE program; Coppola et al., 2019; Bosse et al., 2015; Testor et al., 2019). During the demonstration experiment, a deployment of the Slocum glider was used along the endurance line (MOOSE T00-43 mission) performed from 12 March to 20 June 2020. Table S2 includes information about which sensors the glider was equipped with. Discrete samples were collected from the DYFAMED site in February and March 2020 for comparison with the pCO_2 sensor measurements (Table S4).

The open fixed station W1M3A is located in the Italian EEZ of the Liguro-Provencal basin. Operated by CNR-IAS, the W1M3A consists of a large spar buoy and a subsurface mooring positioned in the immediate vicinity. A detailed description of the observatory can be found in Canepa et al. (2015) and some of this information is found in Table S2. Discrete samples were collected from W1M3A in October 2020 (Table S4).

2.2.2 Adriatic Sea facilities

The fixed station E2M3A is situated in the open sea of the southern Adriatic Sea and is operated by OGS. Information on this site is found in Bozzano et al. (2013) and Ravaioli et al. (2016). In the southern Adriatic, the OGS also regularly operates an ocean glider at the Bari-Dubrovnik section (Mauri et al., 2016; Pirro et al., 2022; Kokkini et al., 2019). During the AT2MED demonstration experiment, the glider transect was extended to include the area of the E2M3A fixed station from 12 June to 2 July 2020. During the 20-day campaign 250 dives between 20 to 950 m profiles separated by 3-5 km and 4-6 hours were collected. Table S2 contains information about the specific sensors mounted at the glider.

In the Gulf of Trieste in the northern Adriatic, the coastal stations PALOMA (operated by CNR-ISMAR) and MIRAMARE (operated by OGS) are situated. Description of the PALOMA station is found in Ravaioli et al. (2016) and Cantoni et al. (2012), while the MIRAMARE site is described in Ravaioli et al. (2016). See Table S2 for information about which sensors are used at the sites. By means of comparing the pCO_2 sensor measurements performed at the sites, discrete carbon samples were collected near PALOMA on 15 July 2020 and in the vicinity of MIRAMARE on 17 July 2020 (Table S4).

2.3 Shipboard data

Discrete samples for Dissolved Inorganic Carbon (DIC) and TA were collected onboard the RV Meteor (M160) during fall 2019 and analysed by GEOMAR. Discrete samples for DIC, TA, pH, and dissolved oxygen are regularly collected next to the fixed ocean stations, however, this was not always possible during the ATL2MED demonstration experiment due to COVID-19 pandemic restrictions. Table S4 gives an overview of the discrete samples collected during the ATL2MED demonstration experiment and their sampling depth and analysing methods.

In addition, salinity was measured continuously on board of the RV Ucadiz at a depth of 2.3 m between 5 and 6 March 2020, when the SD crossed the Gibraltar Strait. Table S2 contains information about the sensor used.

Table 1. Research vessels and fixed ocean stations from which temperature, salinity and/or carbon measurements were compared with those of the SDs.

Research vessel/ fixed station	Position	Institution	SD 1030	SD 1053
RV Meteor	17.80°N 20.60°W	GEOMAR (DE)	30 November 2019	12 December 2019
RV Ucadiz	36.55°N 6.31°W - 36.09°N 5.36°W	UCA (ES)	5-6 March 2020	5-6 March 2020
DYFAMED	43.42°N 7.87°E	CNRS (FR)	28 April 2020	23 April 2020
W1M3A*	43.83°N 9.12°E	CNR-IAS (IT)	29 April-2 May 2020	28 April-2 May 2020
E2M3A*	41.57°N 18.08°E	OGS (IT)	29 June-2 July 2020	29 June-23 July 2020
PALOMA*	45.62°N 13.57°E	CNR-ISMAR (IT)	15 July 2020	15 July 2020
MIRAMARE*	45.70°N 13.71°E	OGS (IT)	17 July 2020	17 July 2020

* These stations are part of the ICOS station network (Steinhoff et al., 2019).

2.4 Argo Float

Float data were retrieved from the Argo Coriolis Global Data Assembly Center in France (GDAC; ftp://ftp.ifremer.fr/argo, Wong et al., 2020). For each Argo float the variable SALINITY ADJUSTED was extracted, and then used for comparison with SD salinity data. Every profile close in space and time (1 day and 30 km) was chosen and then salinity was averaged in the upper 5 m of the water column.

2.5 Model output

The Copernicus Marine Service (CMEMS) model product, specifically the Global Ocean 1/12° Physics Analysis and Forecast (https://doi.org/10.48670/moi-00016) and the Mediterranean Sea Physics Analysis and Forecast (Escudier et al,. 2020, Clementi et al., 2021) were used. Daily data were developed for the global ocean and Mediterranean Sea.

2.6 Satellite product

To evaluate the ocean response, sea surface Chl-a (OCEANCOLOUR_MED_BGC_L3_NRT_009_141), sea surface temperature (Merchant et al., 2019, Buongiorno Nardelli er al., 2022) and the vertical structure of ocean

temperature (MEDSEA_MULTIYEAR_PHY_006_004) were downloaded from the CMEMS data portal and analysed (Table S6 in the Supplementary Material).

3 Methods

3.1 Salinity

Here, the salinity is measured using the PSS-78 scale. During the first transect, T1 (Fig. 2), the two salinity sensors on board the SDs showed high consistency (Fig. 2a, b). After the first maintenance in T2, the SD 1053 showed a reduction in salinity of about 1 compared to the salinity measured by the SD 1030. In T3, the difference in salinity decreased on average to 0.15. During this period, the SDs crossed the Alboran Sea characterised by high thermohaline variability due to the presence of Atlantic and Mediterranean waters (Poulain et al., 2021), and the high spatial and temporal variability in salinity distribution in the area (Capó et al., 2021) complicates the understanding of the observed differences (i.e., sensor error or natural variability). In T4 and T5, salinity shifts of 1 were observed until the end of the experiment.

Given the large variability found in the salinity data of the SDs, a comparison with *in situ* data along the trajectory of the experiment was necessary. We first identified the observing systems (fixed buoy, Argo float) temporally and spatially close to the positions of the SDs. Salinity data, with a temporal and spatial interval lower than 1 day and 30 km, respectively, were used for the comparison and/or correlation, however they were extremely scarce.

To further evaluate the salinity data of the two SDs, a comparison was made with climatological data, considering the closest point in the climatology dataset to the SDs measurements (Fig. 2). SD 1030 exhibited consistent salinity data in periods T1, T2, and T4 ($\Delta S < 0.1$), with deviations observed in periods T3 and T5 (Fig. 2a). Conversely, SD 1053 displayed consistent salinity data only in period T1 ($\Delta S < 0.1$), with higher deviations in periods T2, T3, T4, and T5. Subsequent evaluation of the data distribution characteristics revealed variances between the two SDs (Fig. 2b).

In T5, the climatology failed to represent salinity in Ionian and Adriatic Sea, characterised by a continuous increase in salinity since 2017 (Mauri et al., 2021; Mhianovic et al., 2021; Menna et al., 2022; Neri et al., 2023; Pranic et al., 2023). This was due to the bipolar behaviour of the Ionian Sea, subject to an alternation between the highly saline waters of the Levantine Basin and the less saline waters of Atlantic origin (Pinardi et al., 2019; Gacic et al., 2021; Menna et al., 2022; Civitarese et al., 2023).

To overcome the problem of lack of data, we decided to compare the data acquired by the SDs with the reanalysis model products along the entire route (Fig. 2a, b). The model, while not deviating much from the *in situ* and climatological data (Fig. 2), can provide salinity products along the SD's trajectory allowing to correct the salinity recorded by the SD. Moreover, comparative works between the physical model and experimental observations have shown a satisfactory correlation both in the open ocean (Escudier et al., 2021; Menna et al., 2023) and in the coastal environment (Martellucci et al., 2021). Despite any limitations a model may have in such cases, the use of model products allows a minimum spatial and temporal distance in the comparison of the along track SD measurements. The nearest nodes (in km) with respect to the model data grid to the SD trajectory were chosen. The salinity provided by the model along the two SD trajectories shows very similar values to that measured by SD 1030 (Fig. 3). Salinity differences between the CMEMS model and the SD 1030 observations show a difference less than 0.1 in T1, T2, T4 and T5. During the Alboran Sea crossing (T3), the observed salinity deviated strongly from the model (about 0.6) over only 20 days. In contrast, SD 1053 showed deviating values compared to the model and SD 1030, which cannot be explained by space-time variability. With the exception of T1, the remaining transects (Fig. 3i-j) showed large deviations between model and observed salinities (T2: 0.8, T3: 0.7, T4: 0.9, and T5: 1). This could be related to the long time between the SD 1053 maintenance (early January and early May 2020), but it is more likely that a sensor error occurred in mid-January which even maintenance could not correct.

The salinity correction was performed using a linear regression method in which the salinity data recorded by the autonomous vehicles averaged over the day, were calibrated with the corresponding data from numerical models. A strict criterion, with a significance level of $p < 0.05$ (Table 2), was applied to the correction process.

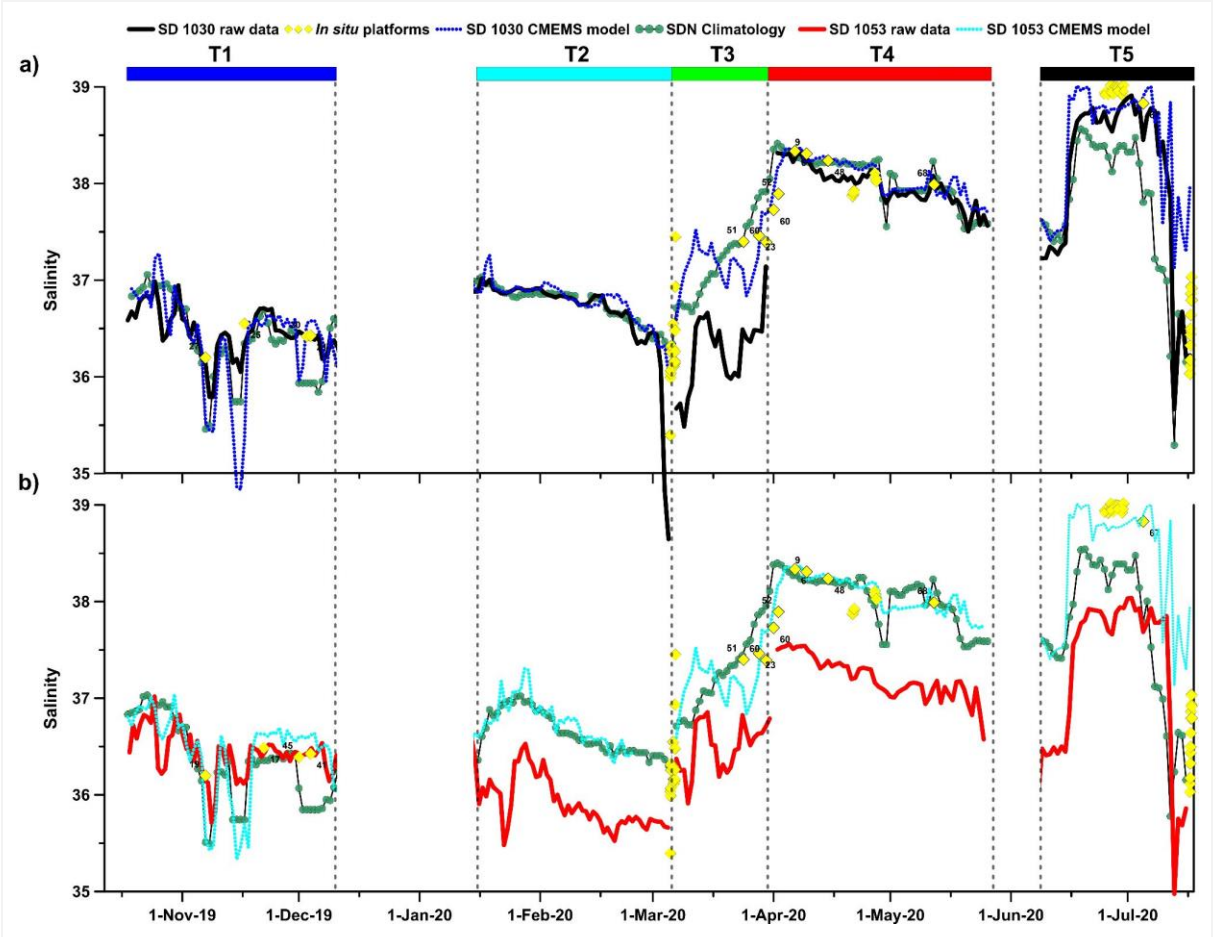

Figure 2. Salinity time series of daily raw data, CMEMS model salinity products, climatology and float data. (a) SD 1030 salinity raw data (black line), model (dotted blue line) and climatological (green circle) data from nearest nodes to the SD trajectory, and *in situ* data (yellow diamonds). (b) SD 1053 salinity raw data (red line), CMEMS model 1053 trajectory (dotted cyan line), climatological data (green circle) and *in situ* platforms (yellow diamonds). Numbers close to diamonds indicate the distance (km) from the trajectory of SD. *In situ* platforms include data from Argo buoys, fixed stations, gliders and RV Ucadiz.

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223 **Table 2. Statistics for the salinity correction. T1, to T5 refer to the different transects, pval is the significance level,**
224 **distribution refers to normal or non normal data distribution, R^2 is the correlation coefficient, RMSE is the root mean**
225 **square error, and NaN refers to lack of data.**

		Direct comparison				
		T1	***T2***	***T3***	***T4***	***T5***
SD 1030	***pval***	0.0007	0.04	<0.001	0.04	0.025
	distribution	non normal	non normal	normal	non normal	normal
	R2	0.59	0.61	0.19	0.71	0.85
	RMSE	-	-	0.9058	-	0.2789

SD 1053	***pval***	0.026	0.003	0.004	<0.001	<0.001
	distribution	non normal	normal	normal	normal	normal
	R2	0.08	0.44	0.25	0.789	0.919
	RMSE	-	0.826	0.7072	0.8444	1.1275

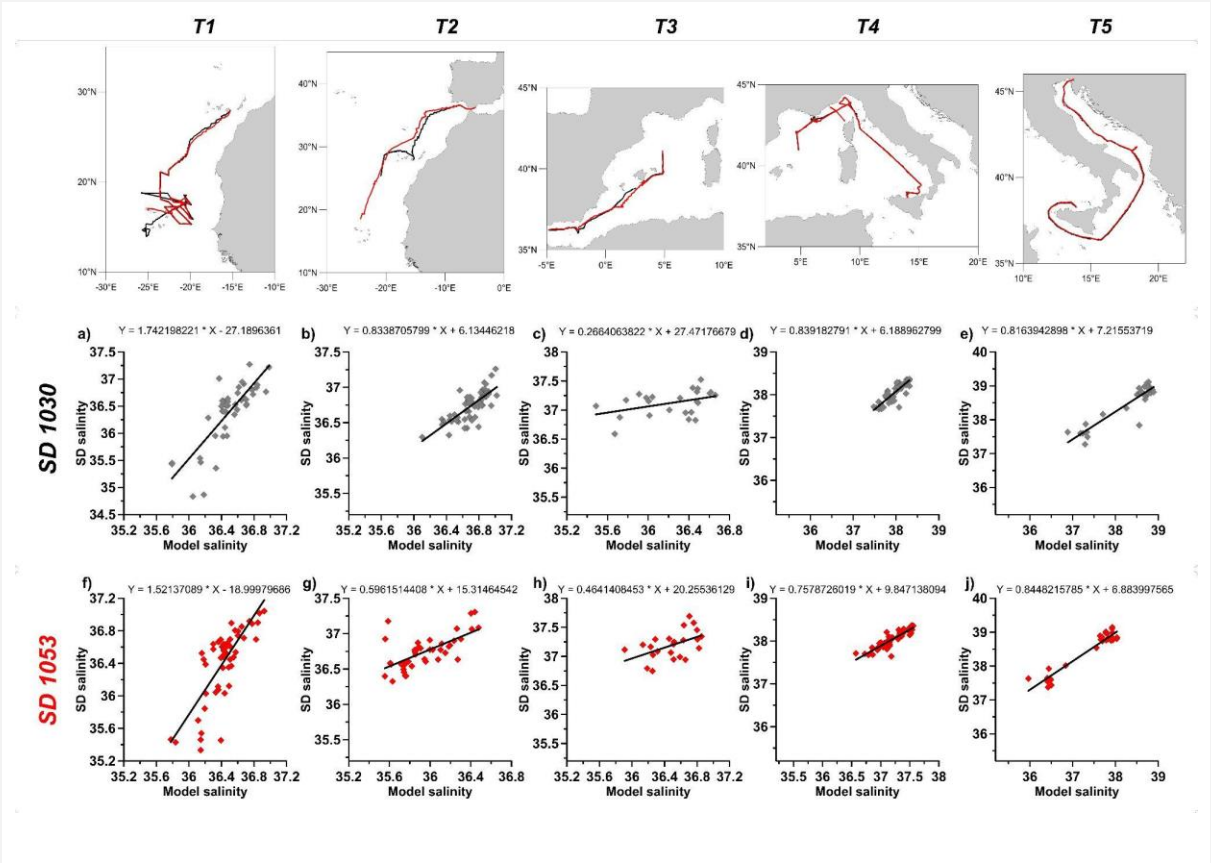

Figure 3. Least square regression between model and SD raw salinity during each transect from T1 (left) to T5 (right) for SD 1030 (a, b, c, d, e) and SD 1053 (f, g, h, i, j). The solid line represents the linear regression fit.

3.2 Dissolved Oxygen

Due to the strong dependence of dissolved oxygen on temperature, we first analyse the temperature along the track of the SDs. During the demonstration experiment, sea temperature (Fig. 4a) showed a seasonal signal similar to those observed at these latitudes (Pastor et al., 2019). The high observed temperature variability also includes the wide geographical coverage of the SDs. The highest temperatures were measured in November 2019 and July 2020 in the tropical Atlantic and the southern Adriatic, respectively. The lowest temperatures were measured in the Gulf of Lion in April 2020. Along the SD tracks, the salinity (Fig. 2b) showed a gradual increase from the Atlantic Ocean to the eastern Mediterranean Sea. Given the correct temperature measurement, any dissolved oxygen drift can be assessed through comparison with dissolved oxygen saturation values. This procedure was

also used to correct Argo float data with climatological observations (Takeshita et al., 2013). The dissolved oxygen saturation showed a gradual decrease from 100% at the start of the demonstration experiment to 80% at the end (Fig. 4c). This behaviour is also reflected in the dissolved oxygen concentration, which decreases by about 40 µmol/kg for SD 1030 and 60 µmol/kg for SD 1053 (Fig. 4b) over the course of nine months with standard deviation of the uncorrected oxygen record of 16 µmol/kg and 72 µmol/kg for SDs 1030 and 1053, respectively.

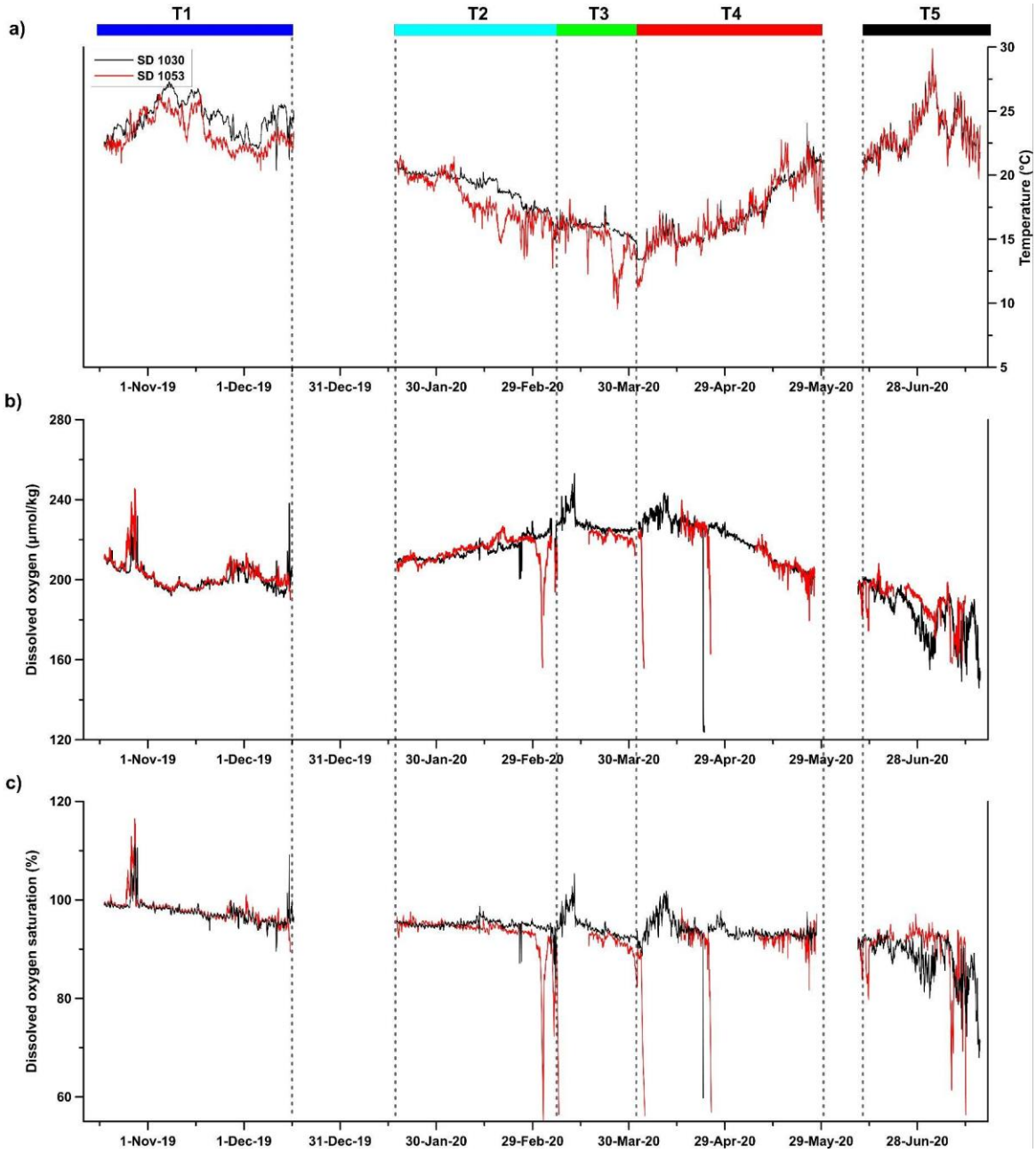

Figure 4. (a) Temperature, (b) dissolved oxygen concentration, and (c) dissolved oxygen saturation for the SD raw data (SD 1030 black line and SD 1053 red line).

Prior to applying correction all the outliers were excluded. After the first analysis we proceeded to correct the dissolved oxygen data, using the same oxygen correction method as used in the Argo program (Bittig et al., 2018). The principle of this method is to compare the dissolved oxygen measurements performed while the Argo oxygen sensor is in air with the oxygen partial pressure (pO_2) in air (Johnson et al., 2015). The latter variable is easily calculated from air temperature, air pressure, and relative humidity acquired by the SDs. Considering that the SD oxygen sensor is installed on the hull about 0.5 m below sea surface and that the SDs sailing cause mixing of the

water surface while sailing, we assume that the SDs oxygen sensors were in equilibrium with the atmosphere above, and furthermore, we can correct for the oxygen sensor drift using the in air calibration method (Bittig et al., 2018; Johnson et al., 2015). Specifically, we computed vapour pressure (V_p, in hPa) from the empirical equation reported in the operating manual of Aanderaa oxygen optode (model 4330) using the air temperature (T_{sd}) recorded from SDs:

$$V_p = e^{(52.57-(\frac{6690.90}{T_{sd}+273.15}))-4.681*ln^{T_{sd}+273.15}} \quad (1)$$

and expected partial pressure (E_{PP}, in hPa) from volume fraction of oxygen (V_{fO2}=0.20946; Glueckauf, 1951), atmospheric pressure (AP_{sd}), vapour pressure (V_p) and relative humidity (RH_{sd}), as follows:

$$E_{PP} = V_{fO2} * (AP_{sd} - (V_p * \frac{RH_{sd}}{100})) \quad (2)$$

The E_{PP} was then compared to the pO_2 from the SDs to compute the gain factor (G) for daily correction.

$$G = \frac{E_{PP}}{pO2_{sd}} \quad (3)$$

The corrected oxygen concentration ($O2_{csd}$) from the SDs was calculated from adjusting the oxygen data from SDs ($O2_{sd}$) with the gain factor.

$$O2_{csd} = G * O2_{sd} \quad (4)$$

For each transect the mean gain was calculated and then, the gain factor was multiplied by the hourly oxygen data allowing to correct the time series.

3.3 Correction and adjustment of pCO_2 data

3.3.1 Fixed-sites pCO_2 data acquisition and qualification

The pCO_2 measurements from the different fixed ocean stations were regularly compared to the pCO_2 calculated from discrete water samples collected by the fixed stations and analysed for TA, pH, and DIC. During the last half of the ATL2MED demonstration experiment, this routine was hampered due to COVID-19 restrictions, thus, between March and July 2020, there were less discrete carbon samples for comparison with fixed station pCO_2. Furthermore, there was minor variability in sampling frequency with regards to the fixed station pCO_2 measurements and in the pair of measured variables used for pCO_2 calculation (TA-pH or DIC-TA) between the different fixed ocean stations (see Table S2 and S4). During the ATL2MED demonstration experiment, DIC, TA, and pH were analysed according to SOP 2, 3b, and 6b, respectively (Dickson et al., 2007) with some minor local variations (Table S4). Certified Reference Material (CRM) and TRIS provided by Prof. A. Dickson (Scripps, USDC, USA) were used to determine the accuracy. pCO_2 was calculated using the speciation software CO2SYS (Pelletier et al., 2007), with the discrete carbon pairs TA-pH or DIC-TA as input variables. In the computation, the carbonate system constants from Lueker et al. (2000), the HSO_4^- constant from Dickson (1990), the total borate-salinity relationship of Lee et al. (2010), and the hydrogen fluoride constant K_F from Perez and Fraga (1987) were used. The uncertainties connected to this calculation ranged from 1.82% when using TA-pH as input variables to 2.65% when DIC-TA were the input variables (Orr et al., 2018). Based on this, no adjustments were performed for the fixed station pCO_2 data when the deviation from pCO_2 calculated from discrete carbon data were less than 7.5 µatm and 10 µatm for the discrete carbon pairs TA-pH and DIC-TA, respectively. Uncertainty thresholds were set based on measurement uncertainties at each facility and temperature and pCO_2 in the vicinity of the fixed stations.

3.3.2 Correction of SD CO_2 data

The general accuracy of the ASVCO2 system attached to the SD 1030 was checked by PMEL prior to deployment by comparing the results with ESRL CO_2 standards traceable to WMO standards (Sutton et al., 2014). For this test, typically 6 standard gases were used. On the return of the ASVCO2 system to PMEL, it was discovered that the span gas was adjusted too low to completely flush the detector and that this had been so during the whole ATL2MED demonstration experiment. Thus, the LI-COR had to be recalibrated at the PMEL lab and this implied that the onboard gas spanning was bypassed, and new calibration coefficients were developed. Furthermore, the pre-mission test data from the PMEL lab were reprocessed using the new calibration coefficients. Based on the reported issues with the ASVCO2 instrument, the accuracy of the CO_2 measurements is estimated to be < 5 µatm.

4 Results and discussion

4.1 Salinity

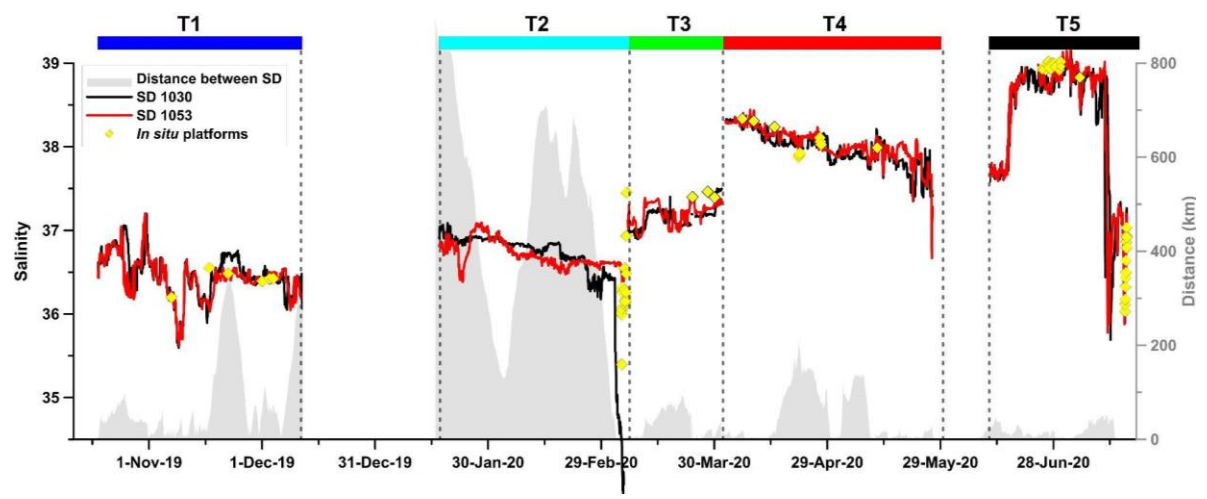

Figure 5. Salinities corrected from SD 1030 (black line), and SD 1053, (red line), and *in situ* platforms (Argo floats, RV Ucadiz, gliders, and fixed stations; yellow diamonds) over the SD trajectory. The shaded grey area indicates the distance (km) between the SD trajectories. The coloured rectangles on top of the figure represent the different transects.

The salinity correction was based on the significant linear correlation (Fig. 3) observed across the different periods (Table 2). The periods characterised by small differences in salinity (<0.1) were not corrected. In general, the corrected salinity for both SDs showed similar values (Fig. 5), and the major differences between the two SDs were mainly due to their temporal and spatial distance. Overall, the correction was largest for SD 1053 (see RMSE values in Table 2). To validate the salinity corrected data a comparison with different observing systems was done.

For SD1030, the corrected salinity data showed a slight overestimation of salinity, while the raw salinity data showed an underestimation. The SD 1030 salinity highlights good agreement in T1 with respect to the SD 1053 (Fig. 5), the average difference was less than 0.05, the highest difference between Argo float data and corrected salinity data observed on 17 November 2019 was ~0.15. In T2, the comparison can only be made for SD 1030 with only one Argo float profile.

Between T2 and T3 a drop in salinity was observed when the SDs crossed the ETNA area, where the salinity exhibits a strong variability (Reverdin et al., 2007), triggered by freshwater flux and eddy transport (Gordon and Giulivi, 2014). This salinity drop was also observed in the climatological data (Fig. 2).

The salinity in T2 (SD 1030) only slightly differed (ΔS ~0.05) with respect to the model and values were in agreement with the observations of the Argo floats during the crossing of the Gibraltar strait. In T3 a significant difference was observed between model and observation (RMSE = 0.906; Table 2), while T4 was in line with the climatology as well as the fixed stations. In T5, the RMSE was 0.279 (Table 2), in the southern Adriatic, the SDs

spent four days sampling the area, which allowed a robust comparison between data from the E2M3A fixed ocean station and the glider measurements. The comparison showed a very good agreement between the observations, which had almost the same salinity. In the northern Adriatic (T5), the comparison with *in situ* data showed the highest differences with respect to the other *in situ* platforms comparison. However, the comparison with the fixed stations (MIRAMARE and PALOMA) showed the same temporal changes with an average difference between the SDs and the MIRAMARE fixed ocean station of ~0.3.

Regarding SD 1053, the comparison with the different fixed ocean stations shows that the corrected salinity in T2, T3, T4 and T5 are consistent with the values measured at the stations (Argo float, glider, buoy, and RV Ucadiz), the differences being mainly due to the distance between the different observatories and to the natural variability of the areas. Also, the corrected data fit well with climatological values and *in situ* platforms. Considering that during T1 the SDs raw data showed a smaller deviation from the Argo float data, the salinity correction was applied after this transect (*i.e.*, from the start of T2).

4.2 Dissolved oxygen

For dissolved oxygen concentration, it would have been preferable to be able to compare the SD data to discrete data. However, over the period of the ATL2MED demonstration experiment, no discrete dissolved oxygen measurements were available due to COVID-19 restrictions. The corrected oxygen measurements (Fig. 6a) spanned from 170 µmol/kg to 270 µmol/kg highlighting the highest concentrations during spring 2020. Time series of percent dissolved oxygen saturation did not show any significant trend (Fig. 6b). Oversaturation was observed at the end of October 2019 (~115%) and at the beginning of March 2020 (~ 105%), while strong undersaturation was observed at 1-2 of April 2020 (~95%) and 8-11 July 2020 (~92%).

Furthermore, we evaluated the change in dissolved oxygen measured by the two SDs in two different geographical areas (the Canary Islands area and the Balearic basin), where dissolved oxygen showed oversaturation (Fig. 7) and undersaturation (Fig. 8). In the first region, we made use of Chl-a data and temperature, while in the second region, temperature was used to evaluate the representativeness of the correction with respect to ecosystem dynamics. The optical sensors on the SDs and thus, the Chl-a measurements, were strongly affected by biofouling for most of the demonstration experiment, which is why we do not use these measurements in this work. However, during the 10 first days in October 2019, the Chl-a data acquired by the SDs seemed to produce reasonable values in accordance with Delory et al. (2018), who found that for new sensors the increase in biofouling needs weeks to become significant. We refer to these Chl-a data, collected by the SDs in the transect T1, when explaining the dissolved oxygen oversaturation episode off the Canary Islands.

The oxygen saturation concentration can be expressed as a function of salinity and temperature, in terms of solubility (Garcia and Gordon, 1992). The gas concentration in seawater depends on thermohaline characteristics and biological activity. The solubility of oxygen decreases with increasing temperature and salinity, showing a strong correlation. In the ocean, dissolved oxygen saturation lower than 100% can be observed during the cold seasons while in the warm season oxygen saturation is higher than 100%, inversely to the dissolved oxygen concentrations (i.e., high concentrations during cold season and low in the warm season). This is because heating and cooling are generally faster than outgassing, except for episodes of high wind speeds which intensifies the air-sea gas exchange (Ulses et al., 2021). Furthermore, dissolved oxygen concentration is affected by primary production and respiration.

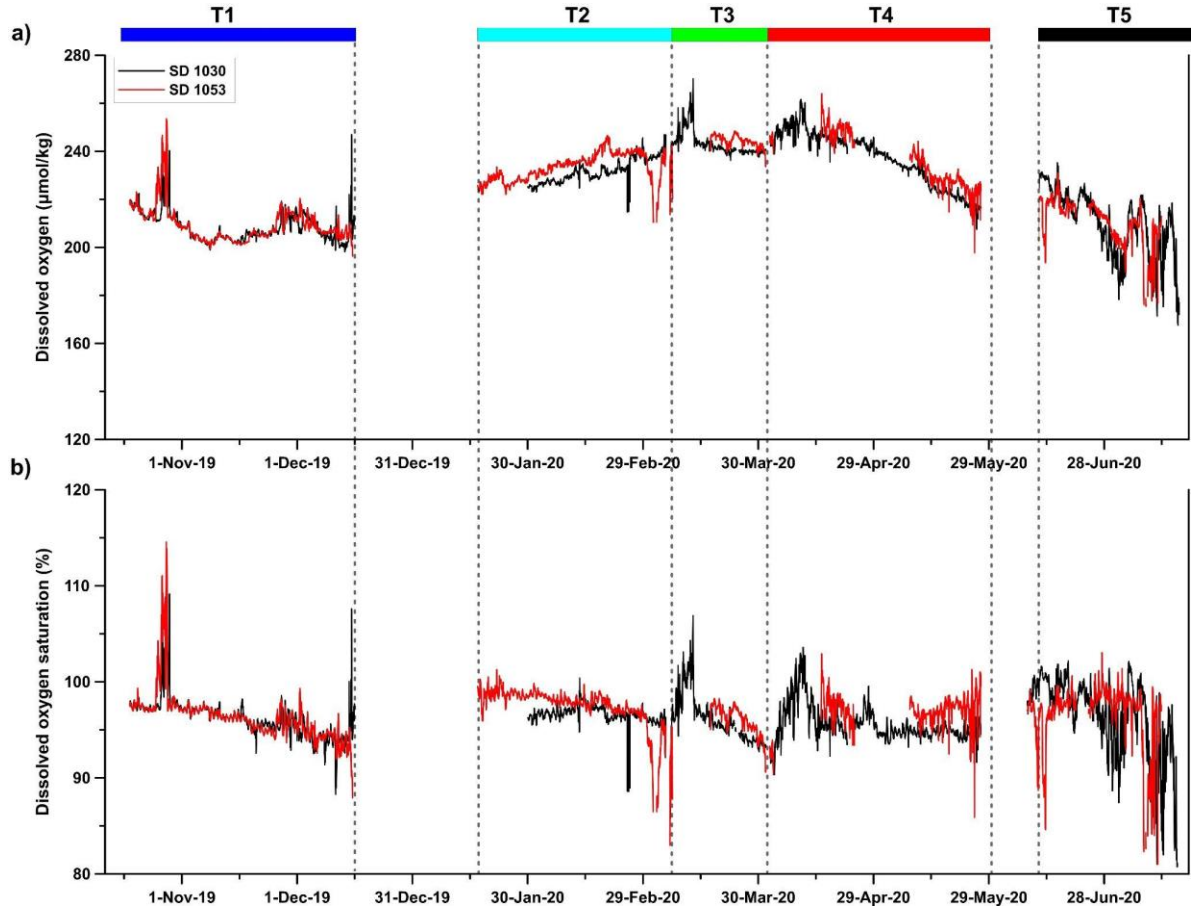

Figure 6. (a) Time series of corrected dissolved oxygen concentration and (b) corrected dissolved oxygen saturation (SD 1030 black line and SD 1053 red line) in percent.

Between October 25 and 29, the dissolved oxygen concentration and saturation were high around the Canary Islands (>240 µmol/kg and >110%; Fig. 7a and b). During the same period high concentrations of Chl-a were measured by SDs (~ 2 µg/l, Fig. 7b, blue and orange line). The area with high Chl-a concentrations off the Canary Islands was visible on the satellite images of sea surface Chl-a concentration (Fig. 7c) and at the same time low sea surface temperature was observed (Fig. 7d). High Chl-a concentrations and low temperatures identify a mesoscale structure that has moved away from the African shelf. Considering that the latter is a very productive area due to the permanent upwelling off NW Africa coast (Cropper et al., 2014; Fischer et al., 2016), this justifies the high Chl-a concentration observed by the SDs at that time.

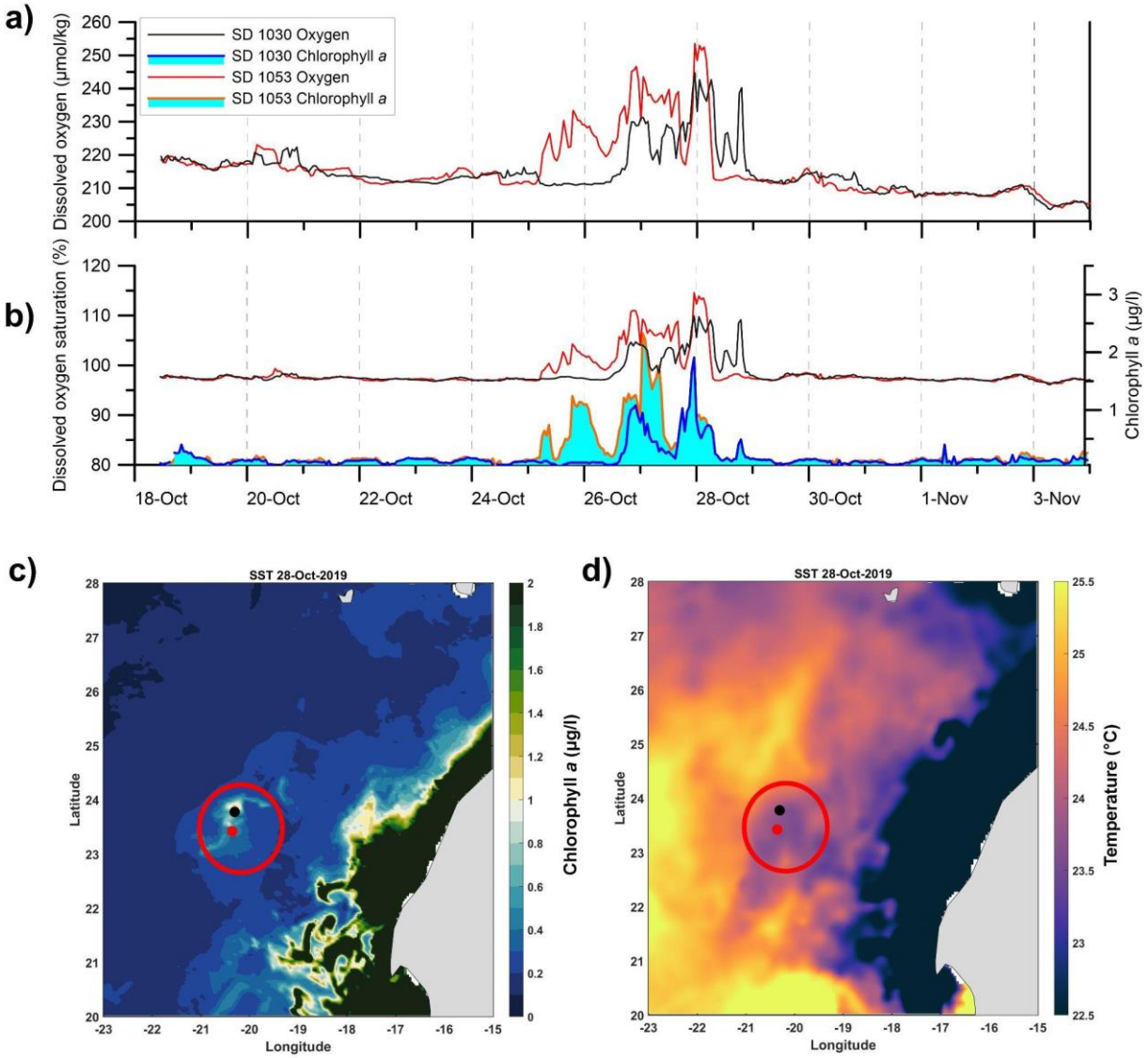

Figure 7. Time series of (a) dissolved oxygen concentration and (b) dissolved oxygen saturation in the Canary Islands area. Sea surface Chl-a concentration (c), and (d) sea surface temperature on 28 October 2019. The red circle highlights the position of SDs (black dot = SD1030 and red dot=SD1053).

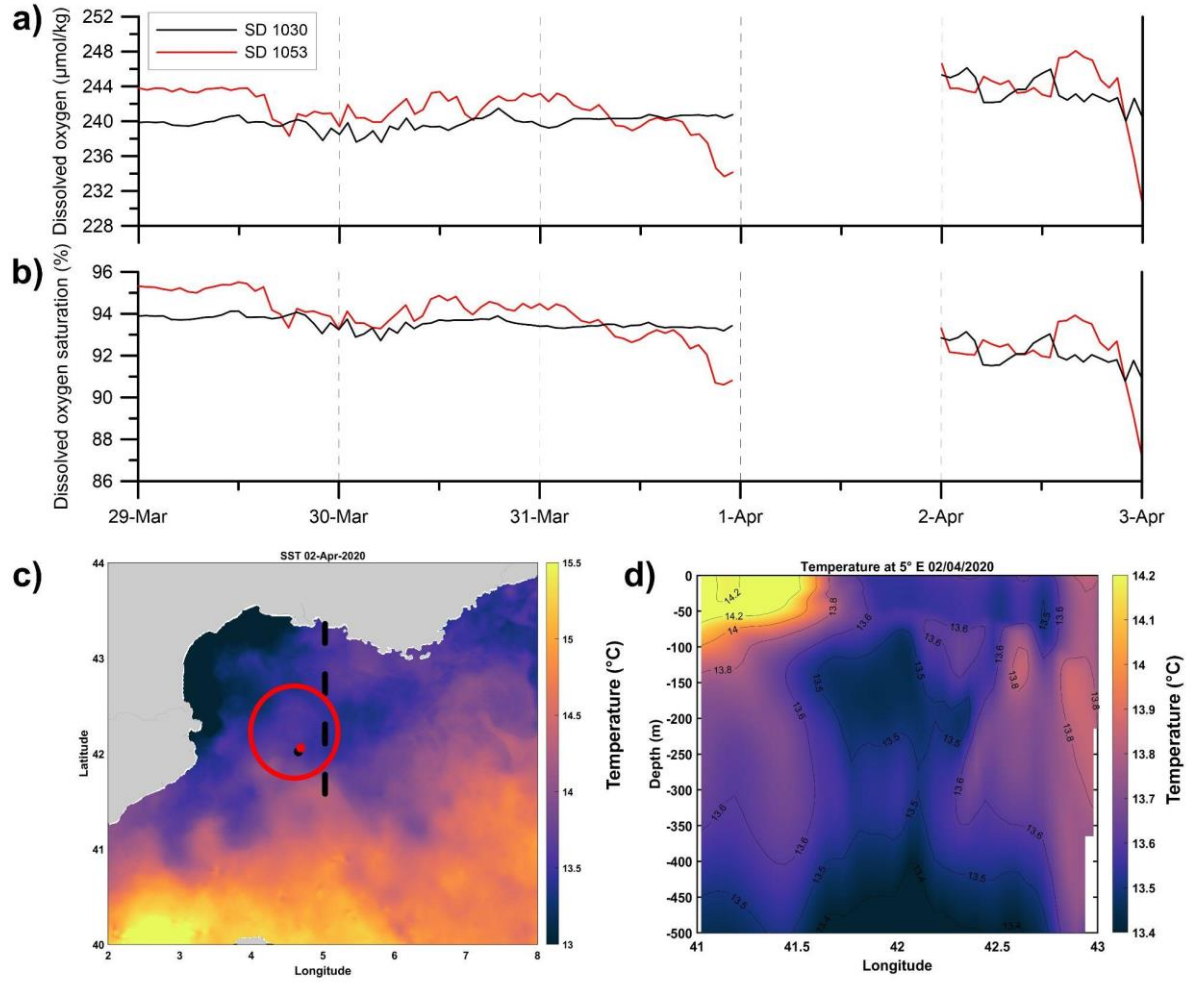

Figure 8. Time series of (a) dissolved oxygen concentration and (b) percent dissolved oxygen saturation in the Balearic basin. (c) Sea surface temperature evolution between 31 March and 2 April 2020. The black dotted line highlights the vertical section in (d). The red circle highlights the position of SDs (black dot = SD1030 and red dot=SD1053).

Between 29 March and 3 April 2020, the SDs crossed the Balearic basin reaching the Gulf of Lion on the 1 April 2020, the SD 1053 measured a decrease in dissolved oxygen concentrations of about 10 µmol/kg (Fig. 8a). This behaviour was also observed in the dissolved oxygen saturation (Fig. 8b) which reached values lower than 95%. The northern part of the basin was characterised by lower surface temperatures (Fig. 8c) than the southern part. The vertical temperature section (Fig. 8d) highlighted the presence of upwelling of cold water to the surface justifying the lower surface temperature observed in Fig. 8c. The presence of this upwelled water caused the decrease in dissolved oxygen saturation (Fig. 8b) observed by the SDs, as the upwelled water is commonly characterised by low dissolved oxygen concentrations due to biological respiration (Chan et al., 2019).

4.3 pCO_2

pCO_2 (in µatm) from the ASVCO2 instrument attached to the SD 1030 were calculated according to Sutton et al. (2014) using T and S from the SBE37-SMP-ODO at the SD. Fig. 9a shows the uncorrected and corrected pCO_2 acquired from the SD 1030. In Fig. 9b, the difference between corrected and uncorrected pCO_2 is shown and the offset increases from approximately 1 µatm at the start of the experiment to approximately 12 µatm at the end.

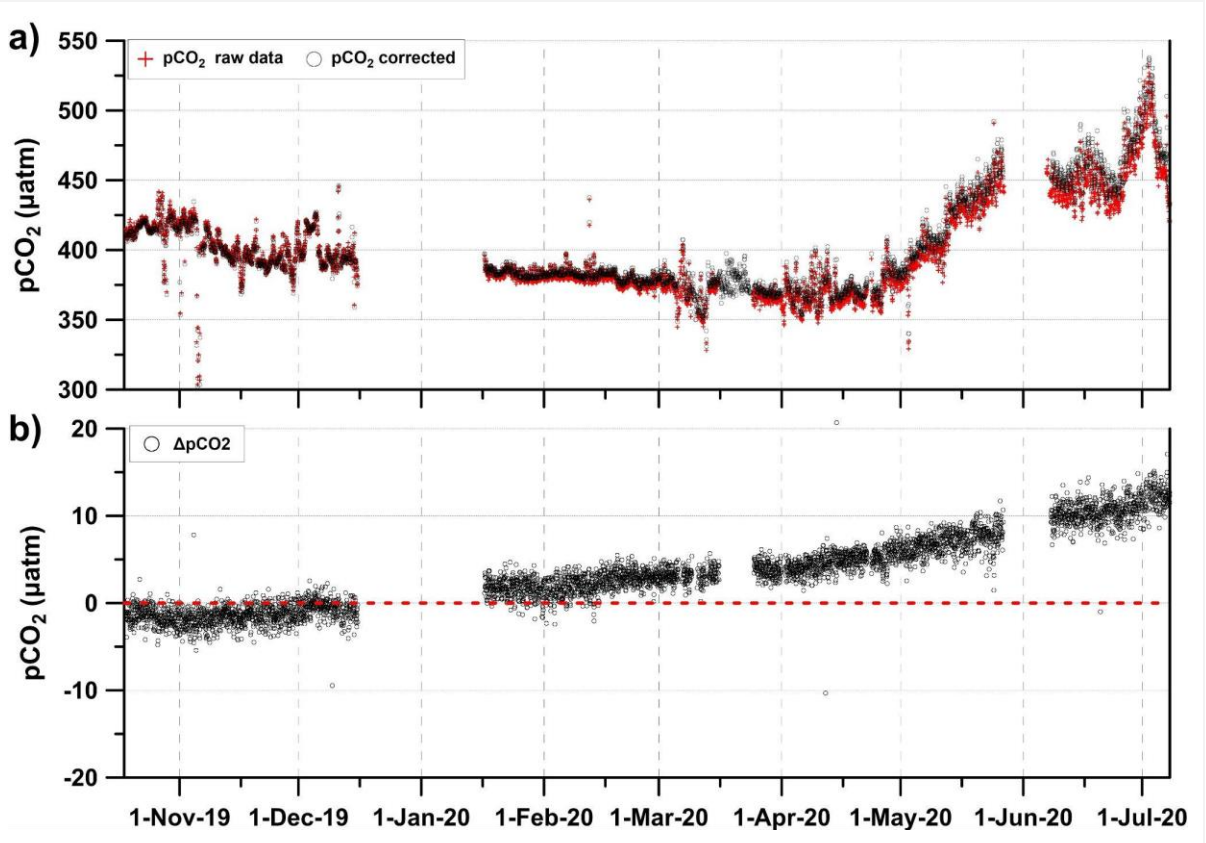

Figure 9. (a) Raw (red crosses) and corrected (black circles) pCO_2 data acquired by the SD 1030 as functions of time. (b) Difference between raw and corrected pCO_2 (ΔpCO_2= corrected pCO_2 - raw pCO_2).

The pCO_2 sensors at the different fixed stations were deployed at depths between 2 to 10 m while the SD measured at 0.5 m depth. To be able to compare pCO_2 measurements from the different depths, the station pCO_2 data were normalised to surface temperature by using the relationship of Takahashi et al. (1993): $pCO_2(1) = pCO_2(2)\ exp^{0.0423\ (T_1 - T_2)}$ (5)

where T is temperature and 1 and 2 refer to the measurements at 0.5 m depth of the SD and at the measurement depth of each local station, respectively. Furthermore, the pCO_2 measurements acquired by the SD 1030 were compared to the corrected pCO_2, surface temperature normalised, from the fixed ocean stations (Fig. 10 and Table 3). The difference varied between -0.5 and -16.9 µatm. The largest difference occurred in the eastern Atlantic, where calculated pCO_2 from discrete DIC and TA were compared to the SD 1030 pCO_2 data. Part of this deviation is likely attributed to calculation errors which is estimated to be about 10 µatm when errors in both DIC, TA, and the carbon constants are included (Orr et al., 2018). The smallest difference between the SD 1030 pCO_2 and the pCO_2 acquired from the fixed stations and normalised to surface temperature are seen at DYFAMED (using DIC and TA as input; Table S4) toward the end of April 2020 (-2.9 µatm) and at MIRAMARE (using pH and TA as input variables; Table S4) in mid July 2020 (-0.5 µatm). The larger discrepancy at W1M3A and PALOMA might be attributed to processes which are not taken into account by temperature normalising, *e.g.*, spatial gradients due to primary production/remineralisation, which would decrease/increase the pCO_2. However, it is difficult to estimate the impact of these processes.

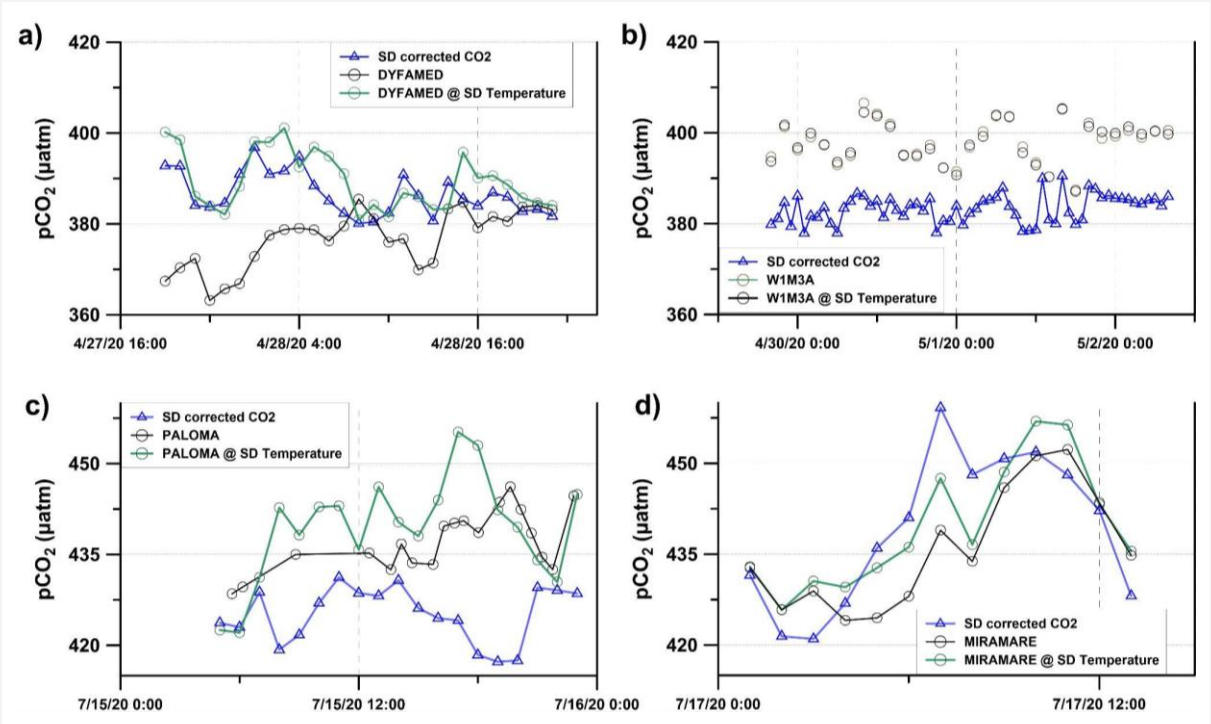

Figure 10. Comparison between pCO_2 measured by the SD 1030 (blue) and at the fixed ocean stations (black and green): the fixed ocean station pCO_2 measured at *in situ* depth and temperature (black) and the fixed ocean station pCO_2 normalised to surface temperature (green). (a) DYFAMED fixed station, (b) W1M3A fixed station, (c) PALOMA fixed station, and (d) MIRAMARE fixed station.

Table 3. Comparison between pCO_2 measurements at SD 1030 and the fixed ocean stations.

Station/ platform	Measurements	Date	Deviation between pCO_2 at SD 1030 and pCO_2 at fixed station normalised to SST (µatm)
RV Meteor	Discrete DIC and TA samples @ 5 m	30 Nov 2019	-16.9 µatm
DYFAMED	pCO_2 sensor @ 10 m	27-28 Apr 2020	-2.9 µatm
W1M3A	pCO_2 sensor @ 6 m	28 Apr - 2 May 2020	-14.2 µatm
PALOMA	pCO_2 sensor @ 3 m	15 July 2020	-14.7 µatm
MIRAMARE	pCO_2 sensor @ 2 m	17 July 2020	-0.5 µatm

SST= sea surface temperature

5 Summary

The ATL2MED demonstration experiment, which lasted for 273 days, represented the first monitoring experiments of SDs covering both the ETNA region and the Mediterranean Sea, evaluating dynamics between fixed ocean stations within the same basin as well as comparing characteristics between basins. The experiment covered all seasons with varying meteorological and oceanographic conditions, primary productivity, and maritime traffic. The ATL2MED lasted longer than planned primarily due to challenges with heavy biofouling of the two SDs, COVID-19 pandemic restrictions, low winds, and strong contrary winds.

A huge amount of data has been produced during the ATL2MED demonstration experiment, and the data required quality control and assurance to a varying degree, primarily depending on how sensitive the sensors were to biofouling. Due to the COVID-19 pandemic restrictions, there was a lack of validation samples collected from

cruise transects, Argo floats, and fixed stations, and this has enforced a new way of thinking regarding drift correction. The SBE salinity data acquired by the SDs have been corrected, when necessary, using model products and the method was validated by comparing the data corrected with available *in situ* measurements. This resulted in remarkable consistency of the salinity correction in both space and time. The data from the Aanderaa dissolved oxygen sensors mounted on the SDs were corrected making use of in air oxygen measurements to correct the trend. The corrected SD datasets fit well with data from fixed stations and gliders, which means that the correction methods used are valid. The output is datasets that are available for process interpretations in future research.

Other SD sensors were affected by biofouling to such a degree that the datasets were unable to be corrected given the limited samples available for validation, like *e.g.* the optical sensors for fluorescence measurements. Some recommendations related to this issue are presented in the next section.

The ATL2MED demonstration experiment is an example of how ASV can be used to perform multi-variable and high-resolution sampling from areas which are not easily accessible, *e.g.* due to remote location, limited shiptime availability, or COVID-19 restrictions. The SDs are environmentally friendly platforms, and they, together with other ASV, are useful as a complement in the validation of fixed ocean stations. However, the experiment clearly shows some of the challenges faced when this type of surface vehicle is part of long-term missions.

6 Experiences and recommendations

Our experiences and recommendations from the ATL2MED demonstration experiment can be summarised in the following bullet points, which are explained in more detail at the end of this paragraph:

We experienced that

- the SD sensors were exposed to severe biofouling
- a substantially amount of effort was required to correct the SD datasets
- some of the SD sensors were mounted in an unfavourable way
- the COVID-19 pandemic limited the access to ship time and thus also collection of discrete validation samples

We recommend to:

- ensure a maintenance and cleaning frequency of the SD sensors and hull which is adapted to the local environment
- use biolimiting equipment at the SDs
- implement an automatic in air calibration procedure for the SD oxygen measurements,
- ensure that the SD sensors are mounted in such a way that they are exposed to open waters
- ensure that a sufficient amount of independent measurements (*e.g.*, salinity, dissolved oxygen, carbonate system, Chl-a) are collected in vicinity of the SD trajectories in order to validate the SD sensors

In general, the use of SDs requires a severe amount of effort into securing that the data are of scientifically usable quality. More specifically, the sensors installed on the SDs always remain in the surface layer and are exposed for biofouling, which can be particularly impacting in relatively warm waters of the Mediterranean Sea, and not only during summer. For future experiment, a maintenance and sensor cleaning frequency depending on the area should be implemented. In situations where this is not possible, biolimiting equipment should be used, like UV systems powered by the solar panels and wipers which regularly clean the optical sensors. Furthermore, regular cleaning of the hull will also ensure the necessary manoeuvrability and navigation precision. Experiences from the ATL2MED demonstration experiment showed that the RBR (https://rbr-global.com/) sensor package used on the SDs had serious issues regarding the biofouling effect. After 9 months in sea, this is somewhat expected. However, the SBE37 sensors seem to be more reliable and robust regarding biofouling, but a regular sensor cleaning procedure is necessary using special devices or human interventions during the SD deployment. Regarding correction of dissolved oxygen, it is advised to facilitate an in-air calibration like the one used for Argo floats. This would require some reorganisation of the sensors; however, it will be easier to correct for drift of the oxygen sensor. It is also advised to look into the location of the SD sensors. For instance, the RBR sensor on the SD 1053 measured significantly lower dissolved oxygen concentration compared to the SBE. One possible explanation for

this could be that the RBR sensor was mounted inside the ship keel where dead water could accelerate the sensor fouling. It must be ensured that the SD sensors are mounted correctly to sample open water.

The ATL2MED demonstration experiment suffered from a lack of discrete samples for validation. Thus, future experiments should be organised in such a way that discrete samples for salinity, dissolved oxygen, carbon, and Chl-a are collected at a reasonable frequency, which will ease the validation of the SD data set quality tremendously. Finally, the suitability of SDs as tool to validate other types of measuring devices (*e.g.*, fixed ocean stations, mobile platforms or ships) strongly depends on various conditions such as distance from the platforms, depth of fixed station measurements, environmental conditions and status of the sensors. All these factors need to be carefully considered to ensure the best possible data set for such a validation.

Data availability. Data described in this work is available from different sources, see Table S6 in the Supplementary Material.

Supplement. The supplementary material is available at the end of this manuscript.

Author contribution. RM, …

Competing interests. The contact author declares that none of the authors has any competing interests.

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Supplementary material

Table S1. Harbours and dates of SD maintenance, of which all took place in 2020.

Place Drone	Mindelo (CV)	Telde, Gran Canaria (ES)	Porquerolles (FR)	Imperia (IT)	Cefalù, Sicily (IT)
SD 1030		12 February	22-23 April		26 May - 6 June
SD 1053	4-14 January			7 May	26 May - 6 June

Table S2. Instruments, sensors, accuracy, and associated measurement frequency at the different fixed ocean stations, gliders, and ship during the ATL2MED demonstration experiment.

Instrument/ sensor	Company/ reference	Variable	Accuracy	Measurement frequency	Used by
SBE37	Sea-Bird Scientific	T Cond	0.002°C, 0.0003 S/m	10/min	DYFAMED
SBE41 (GPCTD)	Sea-Bird Scientific	T Cond	0.002°C, 0.0003 S/m	1/s	Glider MOOSE T00
SBE19	Sea-Bird Scientific.	T Cond	0.005°C, 0.0005 S/m	2/day	MIRAMARE
SBE16 plus v2	Sea-Bird Scientific	T Cond	0.005°C, 0.0005 S/m	12/day	W1M3A
SBE41 (GPCTD)	Sea-Bird Scientific	T Cond	0.002°C, 0.0003 S/m	1/s	Glider South Adriatic
SBE37-SMP-ODO	Sea-Bird Scientific	T Cond	0.002°C, 0.0003 S/m,	15/min 60/min	PALOMA, MIRAMARE

		O_2	3 µmol/kg		
CARIOCA	Merlivat and Brault (1995)	pCO_2	2 µatm	24/day	DYFAMED
CO_2-proCV	Pro-Oceanus Systems Inc	pCO_2	2 µatm	12/day 6/day 24/day	W1M3A E2M3A MIRAMARE
Contros Hydro C systems	4H-JENA engineering GmbH	pCO_2	2 µatm	1/min	PALOMA
SBE21	Sea-Bird Scientific	Cond	0.001 S/m	2/min	RV Ucadiz

T= temperature; Cond=conductivity; O_2=dissolved oxygen; pCO_2=partial pressure of carbon dioxide.

Table S3. Instruments and sensors at the SDs from Saildrone Inc. during the ATL2MED demonstration experiment and used in this work.

Instrument/ sensor	Company/ reference	Variable	Accuracy	Measurement frequency
SBE37-SMP-ODO (SD 1030; SD 1053)	Sea-Bird Scientific	T Cond O_2	0.002°C, 0.0003 S/m, 3 µmol/kg	10/min
ASVCO2 (SD 1030)	PMEL, Sutton et al. (2014)	pCO_2	2 µatm	24/day

T= temperature; Cond=conductivity; O_2=dissolved oxygen; pCO_2=partial pressure of carbon dioxide.

Table S4. Instruments and methods used to analyse discrete samples collected at the RV Meteor and from different fixed stations during the ATL2MED demonstration experiment.

Instrument/ sensor	Company/ reference (SOP)	Variable	Accuracy	# measurements (depth)	Facility
Simultaneous potentiometric acid titration using a closed cell	SNAPO-CO2 prototype, Edmond (1970), Dickson and Goyet (1994)	DIC, TA	± 2 to 5 µmol/kg	1 (5 m)	DYFAMED
SOMMA	UiC (SOP 2), Johnson (1993)	DIC	2 µmol/kg	1 (5 m)	GEOMAR
VINDTA 3S/VINDTA 3C	MARIANDA (SOP 3b)	TA	3 µmol/kg	1 (5 m)	GEOMAR
Automatic potentiometric titrator	Hanna Instruments Titrator HI931	TA	± 4 µmol/kg	3 (6 m)	W1M3A
Automatic potentiometric titrator	Metrohm 685 Dosimat (Hernandez-Aylon, 1999)	TA	3 µmol/kg	5 (0.5, 3 m)[1]	PALOMA
Automatic potentiometric titrator	Mettler Toledo G20/SOP3b	TA	± 4 µmol/kg	10 (0.5, 2 m)	MIRAMARE
pH metre	Mettler Toledo Seven Compact	pH	± 0.001	3 (6 m)	W1M3A
Varian Cary 50 spectrophotometer	Varian, Clayton and Byrne (1993) (SOP 6b)	pH	± 0.003	5 (0.5, 3 m)[2]	PALOMA

Varian Cary 100 Spectrophotometer	Varian, Clayton and Byrne (1993) (SOP 6b)	pH	± 0.002	10 (0.5, 2 m)	MIRAMARE

O_2=dissolved oxygen; DIC=Dissolved Inorganic Carbon; TA=Total Alkalinity.
[1] For each measurement, 2 replicate samples were collected and analysed.
[2] For each measurement, 2 replicate samples were collected and 2-3 analyses were performed at each replicate.
SOP=Standard Operating Procedure according to Dickson et al. (2007).

Table S5. Temperature offsets between SD sensor (SBE37-SMP-ODO) at 0.5 m depth and fixed stations during the ATL2MED demonstration experiment. More details are available in Skjelvan et al. (2021).

Fixed station/ glider	Measurement depth (m)	SD 1030 offset (°C)	SD 1053 offset (°C)
W1M3A	1	-0.006	-0.026
E2M3A	1.7	0.216	0.138
OGS ocean glider	0.5	0.063	0.063
PALOMA	0.5	0.077	0.090
PALOMA	3	-0.061	-0.046
MIRAMARE	0.5	-0.085	-0.205
MIRAMARE	2	-0.117	-0.238

Table S6. Overview over where to find the data used in the current work.

Platform	Variables used in current work	doi or pid	Reference
SD 1030	T, S, O_2, pCO_2	https://hdl.handle.net/11676/QN7XZKcJ2f4kBCGxQEeDdU3P	Skjelvan et al.(2024a)
SD 1053	T, S, O_2	https://hdl.handle.net/11676/9G9rntDvhmu-4nI4w91O11_g,	Skjelvan et al. (2024b)
RV Meteor	T, S, DIC, TA	https://fileshare.icos-cp.eu/s/eyLp9m685QA8ME7	Paulsen et al. (2023)
RV Ucadiz	S	https://fileshare.icos-cp.eu/s/eyLp9m685QA8ME7	Gonzalez and Bruno (2024)
DYFAMED/ BOUSSOLE fixed station	T, S, DIC, TA, pCO_2	https://doi.org/10.17882/43749	Coppola et al., 2023
Nice - Calvi glider	S	https://www.seanoe.org/data/00409/52027/, doi from the MOOSE program (glider SLOCUM Theque on MOOSE T00_43 section)	Testor et al. (2017)
W1M3A fixed station	T, S, pCO_2	https://hdl.handle.net/11676/Z9bGSnVObyglR0o8zcvmIXBz	Bozzano and Pensieri (2024)
E2M3A fixed station	T, S, pCO_2	https://nodc.ogs.it/catalogs/doidetails?4&doi=10.6092/d0d50095-bd30-4ff7-8d0a-a12121e72f78	Cardin et al. (2020)
E2M3A glider	S	https://nodc.ogs.it/catalogs/doidet	Gerin et al. (2021)

		ails?8&doi=10.13120/e7277c6b-444a-4d61-8288-596af1bac3ff	
PALOMA fixed station	T, S, pH, TA, pCO_2	https://hdl.handle.net/11676/an-PJSKTiEVHj3H0gA8ak3lG	Cantoni and Luchetta (2024)
MIRAMARE fixed station	T, S, pH, TA, pCO_2	https://hdl.handle.net/11676/ngPlu-Q0dtDcDx2wMFTNOtnZ	Giani (2024)
Argo buoy	S	https://doi.org/10.48670/moi-00044	Wong et al. (2020)
CMEMS	Model product Chl-a SST Vertical structure of sea temperature	https://doi.org/10.25423/CMCC/MEDSEA_ANALYSISFORECAST_PHY_006_013_EAS7; OCEANCOLOUR_MED_BGC_L3_NRT_009_141, doi: 10.48670/moi-00297; SST_MED_SST_L4_NRT_OBSERVATIONS_010_004, doi:10.48670/moi-00172; MEDSEA_MULTIYEAR_PHY_006_004, doi:10.25423/CMCC/MEDSEA_MULTIYEAR_PHY_006_004_E3R	Clementi et al. (2021)

780 T=temperature; S=salinity; O_2=dissolved oxygen; DIC=Dissolved Inorganic Carbon; TA=Total Alkalinity; pCO_2=partial
781 pressure of carbon dioxide.
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