

Nitrous oxide and methane concentrations and air-sea fluxes in undersampled areas of the Mediterranean basin

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**Abstract:** Nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) are potent greenhouse gases for which oceanic contributions remain uncertain, particularly in undersampled regions like the Southwest and Southeast margins of the Mediterranean Sea, where there is a major observational gap. This data paper presents a comprehensive dataset of monthly N<sub>2</sub>O and CH<sub>4</sub> concentrations and air-sea fluxes collected over a full seasonal cycle (April 2023 - June 2024 at most sites, with one station extended to September 2024) from eight coastal stations across three distinct Mediterranean ecoregions (Alboran, Balearic, and Levantine Seas) as part of the ROADSTER collaborative project. Sampling, preservation, and analytical procedures were standardized across sites, and dissolved-gas analyses were performed in a single laboratory to ensure comparability. We detail standardized sampling and analytical methodologies, including ancillary variables (temperature, salinity, dissolved oxygen, chlorophyll *a* and inorganic nutrients). The compiled dataset reveals distinct seasonal and spatial variability: N<sub>2</sub>O concentrations exhibit a strong negative correlation with temperature, with all stations acting as moderate N<sub>2</sub>O sources. Conversely, CH<sub>4</sub> concentrations show greater variability and a positive correlation with temperature, with the Levantine sub-basin stations displaying episodic high-flux events (up to 35.20 μmol m<sup>-2</sup> d<sup>-1</sup>) indicative of localized seafloor sources. This dataset bridges significant data gaps in the Mediterranean, providing a crucial baseline for regional climate modeling, understanding biogeochemical processes, and future climate change impact assessments.

**Keywords:** Nitrous oxide, Methane, Greenhouse gases data, Mediterranean Sea, Coastal Ocean, Air-sea fluxes, Marine biogeochemistry

## 1. Introduction

40 Methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) play critical roles in the atmospheric radiative balance and the climate system (Ciais et al., 2013). Although their atmospheric budgets are largely controlled by terrestrial sources and sinks, oceanic emissions represent an important component of their global cycling, particularly in coastal regions where emissions of N<sub>2</sub>O and CH<sub>4</sub> are being enhanced (Weber et al., 2019; Sauniois et al., 2020). The last synthesis of greenhouse gases (GHG) fluxes in the global  
45 coastal ocean developed by the Regional Carbon Cycle Assessment and Processes (RECCAP2), evidenced that emissions of CH<sub>4</sub> and N<sub>2</sub>O from the global coastal ocean can offset a substantial fraction of the coastal uptake when expressed in CO<sub>2</sub> equivalent radiative forcing, highlighting the need to consider additionally N<sub>2</sub>O and CH<sub>4</sub> gases when evaluating ocean–climate feedbacks (Rosentreter et al., 2021; Resplandy et al., 2024).

50 The ocean thus acts as both a source and a sink of CH<sub>4</sub> and N<sub>2</sub>O through a range of interacting biogeochemical and microbial processes (Reeburgh, 2007; Codispoti, 2010). Global coastal and oceanic CH<sub>4</sub> emissions are estimated at approximately 12 (6–20) Tg CH<sub>4</sub> yr<sup>-1</sup>, arising from microbially mediated production in marine sediments and the water column, as well as from geological pathways, including hydrothermal vents, cold seeps, mud volcanoes and CH<sub>4</sub> clathrate seepages  
55 (Reeburgh, 2007; Sauniois et al., 2025). As a consequence, coastal ecosystems are increasingly recognised as weak but spatially extensive net sources of CH<sub>4</sub> to the atmosphere (Weber et al., 2019; Sauniois et al., 2020). Similarly, the ocean accounts for about one-third of the natural N<sub>2</sub>O sources to the atmosphere (Ciais et al., 2013). This gas is microbially produced in the ocean mainly through nitrification and denitrification, which are highly sensitive to dissolved oxygen levels,  
60 dissolved inorganic nitrogen (DIN) and redox conditions (Codispoti, 2010; Freing et al., 2012).

In this context, the Mediterranean Sea constitutes a particularly relevant system for investigating marine CH<sub>4</sub> and N<sub>2</sub>O dynamics. As a semi-enclosed basin with an extensive coastline but narrow continental shelf, there are distinct biogeochemical and hydrodynamic characteristics and it is recognised as a climate-change hotspot (MedECC, 2020; Hassoun et al., 2025). Despite accounting  
65 for less than 1% of the global ocean surface, the Mediterranean hosts a disproportionately high biodiversity and is highly vulnerable to global warming, ocean deoxygenation, acidification, and increasing terrestrial nutrient and organic matter inputs, especially in coastal zones (Bianchi and Morri, 2000; Mouillot et al., 2011; Hassoun et al., 2025). These pressures are particularly pronounced in the western Mediterranean, subject to intense coastal development and tourism, that has seen a  
70 dramatic increase in pollution and habitat degradation, with only a small fraction of its coastline remaining in pristine condition (EEA, 2020). Furthermore, the warming rates are not uniform across sub-basins; sea surface temperature warms faster in the Eastern Mediterranean (~0.048 °C/year) than in the Western Mediterranean (~0.036 °C/year) (Pisano et al., 2020). Conversely, the upper

75 water column (5–700 m) warms faster in the Western basin ( $\sim 0.070$  °C/year). Hence, all drivers of  
environmental change are expected to affect future biogeochemical cycles and emissions of  $\text{N}_2\text{O}$   
and  $\text{CH}_4$  in the Mediterranean Sea.

80 Despite its ecological importance and vulnerability, the Mediterranean Sea remains understudied  
regarding non- $\text{CO}_2$  GHG emissions. Data availability of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  and is extremely scarce  
compared to other oceanographic regions, as evidenced by the RECCAP2 synthesis report of GHG  
in global coastal oceans, with only a few measurements available for the emission computations of  
 $\text{N}_2\text{O}$  and  $\text{CH}_4$  (Resplandy et al., 2024). Also, previous studies assessing the  $\text{N}_2\text{O}$  and  $\text{CH}_4$  patterns  
throughout the water column are limited to the western limit of the Mediterranean Basin, namely at  
the Gibraltar Strait, where the impact of vertical mixing at surface  $\text{N}_2\text{O}$  concentrations drives short-  
term temporal variability (de la Paz et al., 2015), the Balearic Ocean Acidification Time Series  
85 (BOATS), where monthly observations show interannual and seasonal variability of  $\text{N}_2\text{O}$  and  $\text{CH}_4$   
since 2018 (Flecha et al., 2023; Flecha et al. 2025) and minor  $\text{CH}_4$  source from seagrass meadow  
reported in Corsica (Champenois et al., 2021). Although studies on GHGs' vertical patterns in water  
columns in the Eastern Mediterranean are very limited (Bange et al 1996), there is multiple evidence  
of gas released from geological sources of  $\text{CH}_4$  at the Eastern Mediterranean Seafloor, where there  
90 are gas seepages and mud volcanoes, pointing out the high gas hydrate potential of the Eastern  
Mediterranean Sea (Merey and Longinos, 2019).

Expanding data collection in under-observed marine regions for non- $\text{CO}_2$  greenhouse gases, such  
as  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , is valuable given their significant contributions to global warming and ocean  
95 feedback mechanisms (Bange et al., 2019; Hassoun et al., 2024). In the Mediterranean Sea, data  
scarcity—together with the limited temporal and vertical resolution of existing observations—still  
hampers basin-wide extrapolations and a comprehensive understanding of ocean–atmosphere  
fluxes of these gases (Rosentreter et al., 2023; Resplandy et al., 2024). These observational gaps  
are further compounded by the lack of long-term, sustained resources for key databases such as  
100 MEMENTO, constraining our ability to assess variability and detect trends in  $\text{N}_2\text{O}$  and  $\text{CH}_4$   
distributions and fluxes (Rees et al., 2022).

To bridge these limitations, strengthening coordination among scientists working across the  
Mediterranean basin is essential for improving data coverage and advancing measurements and  
105 predictions of non- $\text{CO}_2$  GHG dynamics (Bange et al., 2019; Hassoun et al., 2022). Standardising  
measurement protocols and ensuring the availability of long-term, high-quality datasets are  
fundamental steps for reducing analytical biases and for improving our understanding of  $\text{N}_2\text{O}$  and  
 $\text{CH}_4$  processes (Wilson et al., 2018; Bange et al., 2019). Establishing a more integrated  
ocean-observing network in the Mediterranean region will enhance the consistency of data collection  
110 and contribute to the development of a Findable, Accessible, Interoperable and Reusable (FAIR;

Tanhua et al., 2019) data baseline. Such harmonised and traceable observations are prerequisite for robust assessments of oceanic greenhouse-gas fluxes, for reducing uncertainties in emission estimates, and for supporting transparent reporting under international and regional policy frameworks, including the Paris Agreement and its Global Stocktake (UNFCCC, 2015; UNFCCC, 2023).

As a product of the collaborative project between Eastern and Western Mediterranean countries entitled “Greenhouse Gas dynamics on the southern coasts of the Mediterranean Sea” (ROADSTER), this study provides a comprehensive dataset of monthly N<sub>2</sub>O and CH<sub>4</sub> concentrations and fluxes across vast, understudied areas of the Mediterranean Sea—the southwest and southeast margins—over a full seasonal cycle. All gas measurements in seawater were performed in the same laboratory, and sampling and storage protocols were standardised across participants to minimise analytical bias (Wilson et al., 2018). This dataset offers the first combined assessment of seasonal and temporal variability of N<sub>2</sub>O and CH<sub>4</sub> across three Mediterranean ecoregions, providing a robust baseline for understanding the processes driving temporal variability, informing future sampling strategies, and supporting global biogeochemical modelling and upscaling efforts aimed at refining estimates of oceanic CH<sub>4</sub> and N<sub>2</sub>O emissions under ongoing climate and ocean-warming conditions.

## 2. Methods

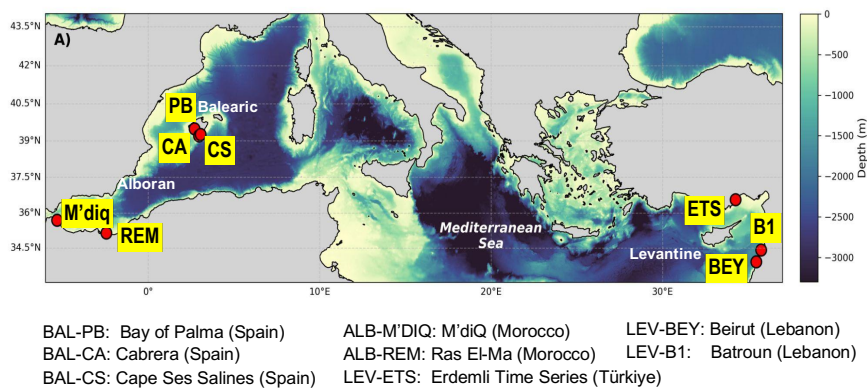
The ROADSTER project, involving various research institutions from countries bordering the Mediterranean Sea (namely Lebanon, Morocco, Türkiye, and Spain), aimed to conduct a year-long series of monthly surface water measurements of N<sub>2</sub>O and CH<sub>4</sub> at established coastal oceanographic stations. Sampling was conducted monthly at eight oceanographic stations across the Mediterranean, which were categorised into three marine regions: the Levantine Sea (Lebanon: LEV-B1, LEV-BEY2, and Türkiye: LEV-ETS), Balearic Sea (Spain: BAL-CA, BAL-CS, and BAL-PB), and Alboran Sea (Morocco: ALB-M'DIQ and ALB-REM).

Measurements encompassed dissolved N<sub>2</sub>O and CH<sub>4</sub>, along with ancillary variables pertinent to the biogeochemical cycles of N<sub>2</sub>O and CH<sub>4</sub>, such as temperature (T), salinity (S), dissolved oxygen (O<sub>2</sub>), chlorophyll *a* (Chl<sub>a</sub>), and inorganic nutrients (nitrite, nitrate, phosphate and silicate). At the start of the project, detailed standardised protocols for the collection, preservation, and storage of gas samples until analysis were disseminated to participating laboratories. Additionally, the standardised equipment for gas sampling were distributed to ensure methodological consistency across participating laboratories and sampling initiatives.

### 2.1 Site description and sampling strategy

### 2.1.1 Morocco

The Mediterranean coast of Morocco was surveyed for 13 months from April 2023 to May 2024 at two sites, which are conditioned by the public health protection vocation of the INRH (National Institute for Fisheries Research) network, i.e. in the vicinity of shellfish production areas in the coastal domain. The stations, namely ALB-M'DIQ and ALB-REM, are located in the region of the Alboran Sea, characterised by the entrance of surface North Atlantic Water in the upper layer entering to the Mediterranean coinciding with the outflow of Mediterranean Water at the deeper layer, and the consistent presence of eddies and coastal upwelling that are modulated by mesoscale wind regime and complex hydrodynamics in the nearby Strait of Gibraltar (Macias et al, 2006).



**Figure 1.** Map of the Mediterranean Sea showing the locations of sampling sites (red dots) and the acronyms used in the text.

The ALB-M'DIQ station is characterized by a typically Mediterranean climate, influenced by offshore Mediterranean water masses and by episodic deep-water upwelling, with an annual mean temperature of 12.5°C and an annual total precipitation of 143 mm in 2023 (<https://fr.tutiempo.net/climat/ws-603400.html>). The site is located 800 m from the coast, with 10 m bottom depth, and was characterized by the highest content of sandy-silt, with no vegetation. The site is near the fishing harbor and marina in the town of M'diq, with a population of c. 100.000, and is subject to various anthropic pressures such as aquaculture activities and to effluent discharges, especially in summer.

The ALB-REM station is located in the north-east of Morocco, with a typically Mediterranean and dry climate, an annual mean temperature of 19.9°C and an annual total precipitation of 374 mm in 2023 (<https://fr.tutiempo.net/climat/ws-603400.html>). The site is located 1 km from the coast, over 30 m bottom depth and on a continental shelf with a gentle slope, consisting of sandy bottom without any vegetation, and 10 km west of the estuary of the Moulouya river (600 km long and the second largest

in the North African coast only behind the Nile Delta). The site is near the fishing harbor of the Ras El-Ma village with a population of c. 20.000. Both sites are close to ports and fish farms.

Samples for N<sub>2</sub>O and CH<sub>4</sub>, Chl *a*, and inorganic nutrients were collected onboard an INRH small vessel. Water samples were collected using Niskin bottles at a depth of approximately 1 m. Hydrological parameters were measured using a Pro DSS Multiparametric sensor (Table 1).

### 2.1.2 Spain

Physicochemical and biogeochemical data were collected from three stations in the Balearic Sea, part of the Balearic Ocean Acidification Time Series (Flecha et al., 2022). The first station, located in the Bay of Palma (BAL-PB: ~30 m bottom depth), is part of the Balearic Islands Coastal Observing and Forecasting System monitoring network (SOCIB; <https://www.socib.es/>). Hourly measurements of temperature, salinity and O<sub>2</sub> were recorded with autonomous sensors. The second station is located in the Bay of Santa Maria, Cabrera Archipelago National Park (BAL-CA: ~8 m depth), a pristine area under governmental protection. Similar parameters (temperature, salinity, pH and O<sub>2</sub>) were measured with high-precision sensors. Both BAL-PB and BAL-CA are fixed monitoring stations, with data collected monthly from depths of 1 and 4 m, respectively. The third site is in the coastal area near the Cape Ses Salines lighthouse (BAL-CS: ~2 m bottom depth), where surface water samples were collected biweekly, starting in August 2022 for O<sub>2</sub> measurements. Samples for dissolved CH<sub>4</sub> and N<sub>2</sub>O concentrations and inorganic nutrients were also collected at all sites. Inorganic nutrient samples were analyzed using the Autoanalyser AA3 HR (Seal Analytical) via continuous-flow analysis. The precision, estimated from the coefficient of variation based on replicate analyses of the same water samples (n = 10), ranged from 0.13 % to 0.5 %.

The BOATS network surface layer is characterized by Modified Atlantic Water (MAW). There is no continuous freshwater contribution or significant anthropogenic pressures in BAL-CA or BAL-CS. Although BAL-PB could be affected by anthropogenic activities due to its proximity to urban areas, previous data analysis in this time series show no significant differences among stations for N<sub>2</sub>O and CH<sub>4</sub> (Flecha et al., 2023; Flecha et al., 2025). Water samples were collected at BAL-PB and BAL-CA using a water pump and at BAL-CS directly from the coast (Table 1).

### 2.1.3 Lebanon

Samples in Lebanon were collected from two coastal stations: 1) LEV-B1 is located offshore Batroun city, Northern Lebanon (Table 1, Fig. 1) and is an inshore time-series station close to Batroun's port with a maximum depth of ~8 m, 2) LEV-BEY is a coastal station located offshore of Beirut, the Lebanese capital, and is surrounded by many infrastructure facilities (mainly recreational ones). Monthly monitoring of key physic-chemical parameters has been conducted since 1991 at station LEV-B1 (Hassoun et al., 2021) and for 30 years ago at station LEV-BEY. Both stations are sampled

on a monthly basis and include measurements of a broad range of physical, chemical, and biological parameters. In addition, analysis of temperature records since 1999 indicates a significant warming trend of approximately 0.09 °C per year (Ouba et al., 2016).

The thermohaline properties were similar to those of the Levantine Sea Water source type. Sampling was conducted monthly between May 2023 and June 2024 to collect surface water samples. *In situ* temperature measurements were conducted using a standard surface thermometer. Salinity was determined using a Beckman salinometer, model R S7-C, with a precision of  $\pm 0.01^{\circ}\text{C}$  for temperature and  $\pm 0.1$  for salinity. For  $\text{O}_2$  analysis, samples were first extracted from the Niskin bottle and concentrations were determined using Winkler titration (Hansen, 1999), with a precision of  $\pm 15 \mu\text{mol kg}^{-1}$ . Phosphate concentrations were measured according to the method described by Murphy and Riley (1962) using a ThermoSpectronic Helios spectrophotometer, with a precision of  $\pm 0.015 \mu\text{mol kg}^{-1}$ . Nitrites ( $\text{N-NO}_2$ ) based on the method described by Bendishneider and Robinson (1952) and Nitrates ( $\text{N-NO}_3$ ) following the method of Strickland and Parsons (1968), with a small modification from Grasshoff, (1961). Samples for total Chl *a* were filtered (Whatman GF/C) at a low pressure, and pigments were then extracted in 90% acetone and determined by a spectrophotometer according to Lorenzen (1967).

In LEV-B1 and LEV-BEY, observed biogeochemical variability is strongly influenced by seasonal and interannual changes in phytoplankton biomass, organic matter cycling, and episodic nutrient inputs. Previous studies in Lebanese coastal waters show recurrent spring and autumn chlorophyll-*a* maxima, reflecting enhanced primary production driven by winter mixing, transitional stratification, and episodic nutrient supply (Ouba et al., 2016). In addition, land-derived nutrient and organic matter inputs, including river discharge, coastal runoff, and wastewater effluents, have been identified as important local drivers modulating productivity and biogeochemical signals along the Lebanese margin (Abboud-Abi Saab et al., 2012; Hassoun et al., 2019).

#### 2.1.4 Türkiye

Seawater samples were collected at the most Eastern Mediterranean coast of Türkiye (LEV-ETS), a highly oligotrophic area, dominated by the Asian Minor Current flowing from east to west in the offshore waters (Fach et al. 2021). The LEV-ETS station is situated 600 meters from the coastline, at a depth of 25 m, on a continental shelf characterized by a gentle slope and a sandy bottom devoid of vegetation. It is located near the town of Erdemli, which has a population of approximately 150,000. The area is subject to coastal eutrophication due to urban and agricultural pressures from the surrounding catchment area. The site is located 800 m east of Lamas River with an annual average discharge of  $2.3 \text{ m}^3 \text{ s}^{-1}$  between 2010-2015 (General Directorate of State Water Affairs). The site has a hot, dry Mediterranean climate with an annual mean temperature of 19°C and an

260 annual total precipitation of 569 mm (Turkish State Meteorological Service, 2024,  
 https://mgm.gov.tr/, accessed August 1, 2024). The site has been monitored monthly between June  
 2023 to September 2024 by METU Institute of Marine Sciences. Based on a ten-year average of  
 physic-chemical measurements (n = 2735), the site is characterized by a  $22.65 \pm 4.7$  °C water  
 temperature,  $39.02 \pm 0.63$  salinity,  $\pm 225.6 \pm 24.3$   $\mu\text{mol kg}^{-1}$  for O<sub>2</sub>,  $0.86 \pm 0.96$   $\mu\text{M}$  for DIN and  
 265  $0.38 \pm 0.35$   $\mu\text{g L}^{-1}$  for Chl *a*. The samplings cruises were conducted onboard RV-Lamas and water  
 samples were collected using Niskin bottles at c. 1-2 m depth. CTD casts were made using Seabird  
 or YSI Exo2 sensors. Due to logistical issues with the CTD, there are certain months (n=5) with  
 missing salinity and temperature. The N<sub>2</sub>O and CH<sub>4</sub> gas samples from these specific cruises were  
 still taken into consideration in our study while temperature and salinity were filled with data from the  
 270 Mediterranean Sea Physical Reanalysis Product (MEDSEA\_MULTIYEAR\_PHY\_006\_004; Escudier  
 et al., 2020) and compared with the climatological time series of temperature and salinity, with good  
 agreement.

**Table 1.** Country, station code and nearest city and code of the sampling sites, geographic  
 275 coordinates, sampling period for N<sub>2</sub>O and CH<sub>4</sub>, number of cruises, ancillary variables.

| Country<br>Oceanogr<br>aphic<br>region | Site<br>Station Code              | Location             | Bottom<br>Depth<br>(m) | Gases<br>Sampling<br>period | Sampling<br>cruises (n) | Ancillary<br>Variables                       | Research<br>Institution<br>cruises |
|----------------------------------------|-----------------------------------|----------------------|------------------------|-----------------------------|-------------------------|----------------------------------------------|------------------------------------|
| Spain<br>Balearic Sea                  | Cabrera<br>BAL-CA                 | 39.15 °N<br>2.95 °E  | 8                      | 05/2023<br>06/2024          | 13                      | T, S, Nuts,<br>O <sub>2</sub> , Chl <i>a</i> | IMEDEA-<br>CSIC                    |
|                                        | Cape Salines<br>BAL-CS            | 39.27 °N<br>3.05 °E  | 2                      | 05/2023<br>06/2024          | 13                      | T, S, Nuts,<br>O <sub>2</sub> , Chl <i>a</i> | IMEDEA-<br>CSIC                    |
|                                        | Palma Bay<br>BAL-PB               | 39.49 °N<br>2.70 °E  | 30                     | 05/2023<br>06/2024          | 13                      | T, S, Nuts,<br>O <sub>2</sub> , Chl <i>a</i> | IMEDEA-<br>CSIC                    |
| Lebanon<br>Levantine Sea               | Batroun<br>LEV-B1                 | 34.42 °N<br>35.75 °E | 8                      | 05/2023<br>06/2024          | 12                      | T, S, Nuts,<br>O <sub>2</sub> , Chl <i>a</i> | CNRS-L                             |
|                                        | Beirut<br>LEV-BEY                 | 33.90 °N<br>35.47 °E | 3                      | 05/2023<br>06/2024          | 14                      | T, S, Nuts,<br>Chl <i>a</i>                  | CNRS-L                             |
| Türkiye<br>Levantine<br>Sea            | Erdemli Time<br>Series<br>LEV-ETS | 36.56 °N<br>34.25 °E | 25                     | 06/2023<br>09/2024          | 12                      | T, S                                         | METU-IMS                           |
| Morocco<br>Alboran Sea                 | M'diq<br>ALB- M'diq               | 35.69 °N<br>-5.32 °E | 10                     | 04/2023<br>04/2024          | 13                      | T, S, Nuts,<br>O <sub>2</sub> , Chl <i>a</i> | INRH                               |
|                                        | Ras El Ma<br>ALB-REM              | 35.15 °N<br>-2.45 °E | 30                     | 04/2023<br>04/2024          | 13                      | T, S, Nuts,<br>O <sub>2</sub> , Chl <i>a</i> | INRH                               |

## 2.2 Dissolved N<sub>2</sub>O and CH<sub>4</sub> measurements

To ensure consistency across all sites, identical sampling materials and detailed protocols for N<sub>2</sub>O and CH<sub>4</sub> were prepared and distributed to each collaborating laboratory. Before the start of the sampling cruises, dedicated training sessions on trace gas sampling were provided to all teams, aiming to harmonize procedures and minimize potential biases between sites and laboratories. Duplicate samples for N<sub>2</sub>O and CH<sub>4</sub> were collected in 120 mL borosilicate serum vials, sealed with grey chlorobutyl septa and aluminium crimps. To preserve the samples, approximately 200 µL of saturated HgCl<sub>2</sub> solution was added and the vials were stored upside down in the dark until analysis at the AQUANITROMET laboratory (de la Paz and Pérez, 2026) of the Instituto de Investigaciones Marinas (IIM-CSIC, Vigo, Spain).

The dissolved concentrations of N<sub>2</sub>O and CH<sub>4</sub> were analysed using the static-headspace equilibration technique combined with gas chromatography following de la Paz et al., (2015, 2021). It consists of creating a headspace by automatically introducing a volume (20 mL) of ultrapure N<sub>2</sub> gas into the sample vial using a high-precision automatic burette displacing the same volume out of the vial by piercing the septum with two needles. After reaching equilibrium overnight in a temperature-controlled environment, 18 mL of the headspace is automatically extracted using a high-precision burette and injected into a gas chromatograph (Agilent GC 7890-A), where the signal for each gas is separated using two independent Porapak Q-packed columns. Finally, N<sub>2</sub>O is detected with an electron capture detector and CH<sub>4</sub> with a flame ionization detector. For the calibration curve, we used triplicate injections of three combined gas standard mixtures of N<sub>2</sub>O and CH<sub>4</sub> in N<sub>2</sub>, supplied by NOAA (National Oceanic and Atmospheric Administration) (N<sub>2</sub>O:CH<sub>4</sub>=332:1959 ppb) and by AirLiquide France (ratios N<sub>2</sub>O: CH<sub>4</sub>=1000:3000 and 3100:5000 ppb). The precision estimated from the averaged coefficient of variation of duplicates (n=123) for this study was 1% for N<sub>2</sub>O and 4.5% for CH<sub>4</sub>. Instrumental limits of detection (LOD) and quantification (LOQ) for GC were defined as 3 and 10 times the standard deviation of triplicate injections of the lowest standard (NOAA atmospheric level), divided by the calibration slope, respectively. This yielded LOD ranges of 3–10 ppbv for CH<sub>4</sub> and 0.1–2.9 ppbv for N<sub>2</sub>O, and LOQ ranges of 9.8–32.4 ppbv for CH<sub>4</sub> and 0.3–9.7 ppbv for N<sub>2</sub>O. Because dissolved gas analysis is fundamentally constrained by detector sensitivity, conservative methodological limits were calculated by substituting the maximum gas-phase LOD and LOQ values into Eq. 1 for seawater at S = 35 and T = 20 °C. The resulting aqueous LODs were 0.11 nmol L<sup>-1</sup> (CH<sub>4</sub>) and 0.16 nmol L<sup>-1</sup> (N<sub>2</sub>O), with corresponding LOQs of 0.35 nmol L<sup>-1</sup> (CH<sub>4</sub>) and 0.55 nmol L<sup>-1</sup> (N<sub>2</sub>O). This analytical system was intercalibrated with other laboratories, with very good results, as part of activities during the first large international experiment to compare marine N<sub>2</sub>O and CH<sub>4</sub> measurements, organized by the Scientific Committee on Oceanographic Research (Wilson et al., 2018).

The gas concentration using the headspace equilibration was computed following Wilson et al. (2018):

$$C_{meas} [\text{nmol L}^{-1}] = \left( \beta \times P V_{wp} + \frac{xP}{RT} V_{hs} \right) / V_{wp} \quad \text{Eq. 1}$$

where  $\beta$  denotes the Bunsen solubility coefficient of  $\text{N}_2\text{O}$  (Weiss and Price, 1980) and  $\text{CH}_4$  (Wiesenburg and Guinasso, 1979) expressed in  $\text{nmol L}^{-1} \text{atm}^{-1}$ ;  $x$  is the dry gas mole fraction (ppb) determined in the headspace;  $P$  is the ambient atmospheric pressure (atm);  $V_{wp}$  and  $V_{hs}$  are the volumes of the water sample and equilibrated headspace, respectively (mL);  $R$  is the universal gas constant ( $0.08205746 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ); and  $T$  is the equilibration temperature (K). The  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentrations are also expressed as percent saturation ( $\text{N}_2\text{OSat}$  and  $\text{CH}_4\text{Sat}$  in %), calculated as the ratio between the measured concentration ( $C_{meas}$ ) and the equilibrium concentration in seawater ( $C_{equi}$ ) for each gas. The equilibrium concentrations were computed by multiplying Bunsen solubility coefficient ( $\beta$ ) of each gas by the monthly average atmospheric molar fraction of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  measured at the Lampedusa monitoring station—the only site in the Mediterranean Sea with continuous records of these gases—obtained from the NOAA monitoring network (Lan et al., 2025).

Due to the lack of standardised QC tools or reference materials in aqueous phase for  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , such as those available for the carbonate system (CRMs produced by A. Dickson at Scripps USA), our QC procedure relied on duplicates seawater samples and reported results as the coefficient of variation (CV, %). The presence of outliers was established based on the CV value between duplicates; hence, samples were discarded with a CV higher than 4.5% ( $n=3$ ) for  $\text{CH}_4$  and 1% for  $\text{N}_2\text{O}$  ( $n=1$ ). In addition, some glass flasks were broken during transport to Vigo ( $n=14$ ), reducing the total number of duplicates samples.

### 2.3 Calculation of $\text{N}_2\text{O}$ and $\text{CH}_4$ air-sea fluxes

The air-sea fluxes ( $F$ ) were calculated using the following equation:

$$F = k_w (C_{meas} - C_{equi}) \quad \text{Eq. 2}$$

where  $k$  is the gas transfer velocity ( $\text{cm h}^{-1}$ ) and  $(C_{meas} - C_{equi})$  is the air-sea concentration gradient of  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , being  $C_{meas}$  and  $C_{equi}$  the measured and equilibrium gas concentrations defined in the previous section. By convention, and following the sign of the gas concentration gradient, negative values of  $F$  correspond to a transfer of  $\text{N}_2\text{O}$  or  $\text{CH}_4$  from the atmosphere to the ocean (i.e., a sink for the atmosphere) and positive values of  $F$  correspond to a transfer of those gases from the ocean to the atmosphere (i.e., a source for the atmosphere). There is a long-term debate over which is the best expression for gas transfer rate  $k$ , but here we adopted as the expression given by Wanninkhof et al. (2014), since it is widely used in the last RECCAP2 analysis for GHG emissions in the coastal ocean (Resplandy et al., 2024). The gas transfer velocity by Wanninkhof (2014), gave

the expression  $k_w = 0.251 \langle U^2 \rangle (Sc/660)^{-0.5}$ , where  $\langle U^2 \rangle$  is the average of the square wind speed and  $Sc$  is the Schmidt number (dimensionless). For our study, due to lack of local sources for wind data on land or buoy for some of the stations, we used the monthly averaged of the square of 6 hourly wind data provided by the Cross-Calibrated Multi-Platform Ocean Surface Wind Vector 3.0 (CCMP) wind data product that combines satellite and buoy data with model predictions (Mears et al., 2022). This wind speed product is the optimum choice using the  $k$  proposed by Wanninkhof (2014), which is computed using this same data product, and has been demonstrated to be an optimum wind source for coastal regions (Otero et al., 2013). The  $Sc$ , dependent on the temperature, salinity, and specific gas molecule, is calculated according to the coefficients for  $N_2O$  and  $CH_4$  and the equation reported by Wanninkhof (2014). Then, the Schmidt number for the *in situ* salinity at the Mediterranean station was calculated by interpolating  $Sc$  for fresh water and seawater. To determine the annual average air-sea fluxes of  $N_2O$  and  $CH_4$  at each station, calculations were performed over a 12-month period. Missing monthly values of  $N_2O$ ,  $CH_4$ , temperature, and salinity during this timeframe were reconstructed through temporal linear interpolation based on the closest available cruise measurements.

#### 2.4 Analysis of the variability of spatial and temporal variability of $N_2O$ and $CH_4$

To determine whether the differences in  $N_2O$  and  $CH_4$  concentrations and other variables across stations were statistically significant, we used Tukey's test with a significance level of  $p < 0.05$ . Additionally, we compute the Spearman correlation coefficients between surface water  $CH_4$  and  $N_2O$  concentrations and potential environmental factors, such as water temperature, salinity, dissolved oxygen, inorganic nutrients, and Chl *a*. All analyses were done using the R software.

### 3. Results

Besides specific  $N_2O$  and  $CH_4$  measurements, we detail the environmental setting and primary oceanographic processes influencing the variability of measurements conducted in our study, while also providing initial insights for future in-depth biogeochemical studies in the region.

A total of 111 observations of  $N_2O$  and  $CH_4$  were obtained between April 2023 and June 2024 (except for LEV-ETS, where observations were extended to September 2024), accompanied by measurements of temperature, salinity, dissolved oxygen, Chl *a*, and nutrients ( $NO_3$ ,  $NO_2$ ,  $PO_4$ , and  $SiO_2$ ). Temporal coverage is uniform across stations, with one sampling event per month, except for minor gaps due to logistical problems with ship availability or inclement weather.

### 3.1. Seasonal variability of N<sub>2</sub>O and CH<sub>4</sub> concentrations

Overall, the seasonal variability of sea surface temperature (SST) was very similar in every region, ranging from 14.5 °C in BAL-PB (March 2024) to 31.2 °C in LEV-BEY (August 2023) (Fig. 2). ALB-M'DIQ exhibits unique characteristics, particularly the unexpectedly low temperatures observed during the summer. These anomalies are likely linked to the eddy-driven vertical motion in the Alboran sub-basin. This connection is supported by several studies that have documented mesoscale eddies with intensified vertical motion and subsurface anticyclonic eddies along the African coast (Tintoré et al., 1991; Viudez et al., 1998). Hence, except for ALB-M'diq, the maximum (August) and minimum surface temperatures (from December to March) showed an overall synchronised cycle between the stations, with lower seasonal SST amplitudes in the southern coast of the Alboran sub-basin (9.5 °C ALB-REM) to higher seasonal SST amplitudes in the stations of the Balearic Sea (13.3 °C in BAL-PB).

The sea surface salinity ranged from 36.6 in BAL-CS in June 2024 to 39.5 in LEV-ETS (Fig. 2b). Compared to the other regions, the seasonal cycle of salinity was clearly observed in the surface waters of Lebanon, where both stations LEV-B1 and LEV-BEY showed higher salinity values from July to November, owing to intense evaporation and lower values from January to April owing to precipitation/continental runoff (Abboud-Abi Saab et al., 2012).

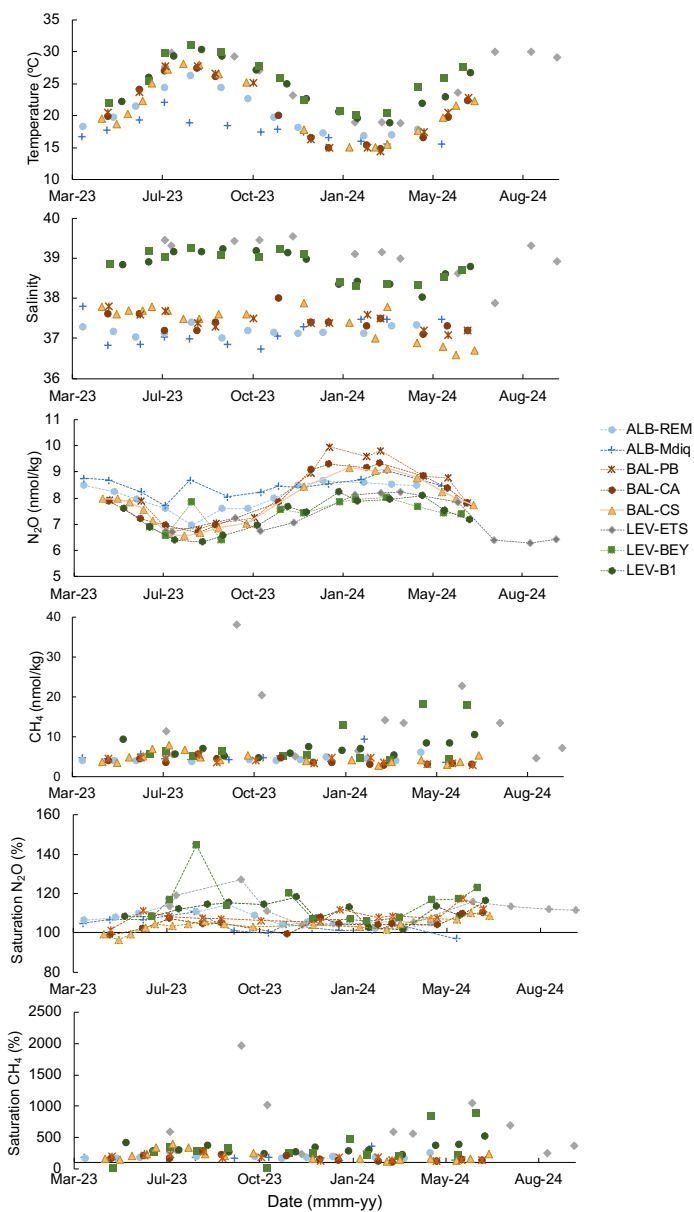
Seasonal variability in N<sub>2</sub>O concentrations was observed at all stations, with concentrations increasing during winter and reaching minimum values in summer (Fig. 2, Table 2). The highest N<sub>2</sub>O concentration of 9.95 nmol kg<sup>-1</sup> was measured in BAL-PB in January 2024, whereas the minimum N<sub>2</sub>O concentration of 6.3 nmol kg<sup>-1</sup> corresponded to LEB-B1 in August of 2023. Monthly N<sub>2</sub>O concentrations showed a clear intra-annual cycle, with amplitudes ranging from 1.3 nmol kg<sup>-1</sup> in ALB-M'DIQ to 3.1 nmol kg<sup>-1</sup> in BAL-PB Bay, which were directly correlated with SST amplitude. Despite some inter-station differences, the timing of the peaks and troughs was broadly consistent across the Mediterranean coast.

The CH<sub>4</sub> concentrations in surface waters ranged from 2.9 nmol kg<sup>-1</sup> measured in March 2024 in BAL-CA to 38.2 nmol kg<sup>-1</sup> measured in September 2023 in LEV-ETS (Table 2). The distribution of CH<sub>4</sub> concentrations were very skewed, and the minimum CH<sub>4</sub> was comparable between the stations (60% of values were lower than 5 nmol kg<sup>-1</sup>), and CH<sub>4</sub> peaks were evenly distributed and consistently high along the coast of the Levantine sub-basin. Only BAL-CS showed a moderate seasonal trend, with a gradual increase in CH<sub>4</sub> concentrations in June, peaking in July, and gradually decreasing through September 2023. Apart from this, no clear seasonal pattern was observed for CH<sub>4</sub> concentrations.

The saturation status of N<sub>2</sub>O in surface water for most of the period was oversaturated (Fig. 2, Table 2), except in May 2023 at the stations of the Balearic sub-basin (BAL-CS, BAL-CA) and in ALB-M'DIQ in October 2023 and May 2024 with a moderate seasonal trend of lower N<sub>2</sub>OSat in winter and spring, and higher oversaturation in summer months, with the N<sub>2</sub>OSat ranging from 96 ± 0% in BAL-  
425 CS in May 2023 and 127 ± 1% in LEV-ETS in September 2023. The surface water at all the stations was supersaturated in CH<sub>4</sub> (Fig. 2, Table 2), with minimum values during the winter and early spring (110±4% in BAL-CA in March 2024) and higher values in summer (up to 400%), with very high CH<sub>4</sub>Sat peaks in the eastern Basin of the Levantine sub-basin that reached the 1973 ±4%

**Table 2.** Summary of the results using the entire database. The table shows the average, minimum (min), median, and maximum (max) values for temperature (°C), salinity, dissolved CH<sub>4</sub> concentration (nmol kg<sup>-1</sup>), CH<sub>4</sub> saturation percent (CH<sub>4</sub> Sat %), dissolved N<sub>2</sub>O concentration (nmol kg<sup>-1</sup>), N<sub>2</sub>O saturation percent (N<sub>2</sub>O Sat %) in the surface water for every station

|               |           | Salinity | Temperature<br>(°C) | CH <sub>4</sub><br>(nmol<br>kg <sup>-1</sup> ) | CH <sub>4</sub> Sat<br>(%) | N <sub>2</sub> O<br>(nmol<br>kg <sup>-1</sup> ) | N <sub>2</sub> OSat<br>(%) | Dissolved<br>Oxygen<br>(μmol kg <sup>-1</sup> ) | CH <sub>4</sub> a<br>(mg L <sup>-1</sup> ) | Nitrate<br>(μM) | Nitrite<br>(μM) | Phosphate<br>(μM) | Silicate<br>(μM) |
|---------------|-----------|----------|---------------------|------------------------------------------------|----------------------------|-------------------------------------------------|----------------------------|-------------------------------------------------|--------------------------------------------|-----------------|-----------------|-------------------|------------------|
| Balearic Sea  | BAL-CA    | Mean     | 37.40               | 20.4                                           | 3.8                        | 168                                             | 8.1                        | 105                                             | 228                                        | 0.06            | 0.18 ±          | 0.03              | 0.32             |
|               |           | ±SD      | ±0.24               | ±4.7                                           | ±0.8                       | ±48                                             | ±1.0                       | ±4                                              | ±20                                        | ±0.07           | 0.12            | ±0.04             | ±0.53            |
|               |           | min      | 37.10               | 14.8                                           | 2.9                        | 110                                             | 6.7                        | 98                                              | 195.21                                     | 0.00            | 0.06            | 0.00              | ±0.2             |
|               |           | max      | 38.00               | 27.5                                           | 5.6                        | 277                                             | 9.3                        | 110                                             | 254.83                                     | 0.16            | 0.38            | 0.14              | 0.05             |
|               |           | Mean     | 37.42               | 21.5                                           | 4.7                        | 211                                             | 7.8                        | 104                                             | 235                                        | 0.08 ±          | 1.97 ±          | 0.05 ±            | 1.91             |
|               | BAL-CS    | ±SD      | ±0.42               | ±4.4                                           | ±4.4                       | ±80                                             | ±0.9                       | ±3                                              | ±18                                        | 0.06            | 1.62            | 0.06              | 0.12 ±           |
|               |           | min      | 36.60               | 15.1                                           | 2.9                        | 113                                             | 6.6                        | 9                                               | 209.39                                     | 0.00            | 0.23            | 0.00              | 0.16             |
|               |           | max      | 37.90               | 28.1                                           | 8.0                        | 399                                             | 9.2                        | 110                                             | 259.54                                     | 0.17            | 6.27            | 0.22              | 0.01             |
|               |           | Mean     | 37.44               | 21.1                                           | 4.1                        | 180                                             | 8.3                        | 108                                             | 232 ± 17                                   | 0.08 ±          | 0.36 ±          | 0.06 ±            | 0.70             |
|               |           | ±SD      | ±0.21               | ±5.0                                           | ±0.8                       | ±44                                             | ±1.1                       | ±4                                              | 0.09                                       | 0.47            | 0.05            | 0.23              | 0.18 ±           |
| Balearic Sea  | BAL-PB    | min      | 37.10               | 14.5                                           | 3.0                        | 129                                             | 6.8                        | 101                                             | 208.88                                     | 0.00            | 0.03            | 0.01              | 0.00             |
|               |           | max      | 37.80               | 27.8                                           | 5.5                        | 275                                             | 10.0                       | 117                                             | 254.82                                     | 0.30            | 1.26            | 0.14              | 0.80             |
|               |           | Mean     | 38.80               | 24.5                                           | 6.9                        | 323                                             | 7.3                        | 111                                             | 212                                        | 0.19            | 0.06            | 0.06              | 0.99             |
|               |           | ±SD      | ±0.39               | ±3.8                                           | ±1.7                       | ±80                                             | ±0.6                       | ±5                                              | ±16                                        | ±0.12           | 0.6 ± 0.62      | ±0.04             | ±2               |
|               |           | min      | 38.02               | 18.9                                           | 4.7                        | 223                                             | 6.3                        | 102                                             | 183.49                                     | 0.05            | 0.14            | 0.02              | 0.01             |
| Levantine Sea | LEV-B1    | max      | 39.24               | 30.4                                           | 10.5                       | 516                                             | 8.2                        | 118                                             | 241.98                                     | 0.53            | 2.64            | 0.15              | 6.23             |
|               |           | Mean     | 38.82               | 25.3                                           | 8.1                        | 383                                             | 7.4                        | 116                                             | --                                         | 0.46            | 1.21            | 0.1               | 0.07             |
|               |           | ±SD      | ±0.36               | ±5.7                                           | ±5.2                       | ±243                                            | ±0.5                       | ±11                                             | --                                         | ±0.22           | ±2.03           | ±0.07             | ±0.04            |
|               |           | min      | 38.32               | 20.1                                           | 4.4                        | 192                                             | 6.4                        | 106                                             | --                                         | 0.14            | 0.12            | 0.02              | 0.01             |
|               |           | max      | 39.26               | 31.2                                           | 18.2                       | 900                                             | 8.0                        | 145                                             | --                                         | 0.84            | 7.78            | 0.25              | 0.15             |
| Levantine Sea | LEV-BEY   | Mean     | 38.23               | 24.2                                           | 13.6                       | 659                                             | 7.2                        | 112                                             | --                                         | --              | --              | --                | 6.93             |
|               |           | ±SD      | ±0.46               | 4.6±                                           | ±9.8                       | ±499                                            | ±0.7                       | ±7                                              | --                                         | --              | --              | --                | --               |
|               |           | min      | 38.63               | 18.8                                           | 4.7                        | 237                                             | 6.3                        | 104                                             | --                                         | --              | --              | --                | --               |
|               |           | max      | 39.56               | 29.8                                           | 38.2                       | 1973                                            | 8.2                        | 127                                             | --                                         | --              | --              | --                | --               |
|               |           | Mean     | 37.18               | 17.7                                           | 4.9                        | 199                                             | 8.5                        | 104                                             | 245                                        | 0.27            | 0.44            | 0.09              | 0.07             |
| Alboran Sea   | ALB-MIDIQ | ±SD      | ±0.33               | ±1.8                                           | ±1.5                       | ±56                                             | ±0.3                       | ±4                                              | ±9                                         | ±0.23           | ±0.25           | ±0.1              | ±0.05            |
|               |           | min      | 36.75               | 15.6                                           | 3.6                        | 142                                             | 7.7                        | 97                                              | 231.45                                     | 0.00            | 0.05            | 0.01              | 0.03             |
|               |           | max      | 37.81               | 22.2                                           | 9.3                        | 368                                             | 9.1                        | 111                                             | 255.10                                     | 0.89            | 0.78            | 0.38              | 0.68             |
|               |           | Mean     | 37.18               | 20.3                                           | 4.5                        | 194                                             | 8.1                        | 107                                             | 225                                        | 0.08            | 0.61            | 0.25              | 0.21             |
|               |           | ±SD      | ±0.12               | ±3.2                                           | ±0.8                       | ±37                                             | ±0.5                       | ±4                                              | ±12                                        | ±0.07           | ±0.43           | ±0.28             | 0.1              |
| Alboran Sea   | ALB-REM   | min      | 37.01               | 16.8                                           | 3.9                        | 157                                             | 6.9                        | 102                                             | 202.49                                     | 0.02            | 0.09            | -0.08             | ±0.06            |
|               |           | max      | 37.40               | 26.3                                           | 6.1                        | 259                                             | 8.6                        | 114                                             | 243.68                                     | 0.29            | 1.35            | 0.68              | 0.09             |



**Figure 2.** Time series data from the study sites, from top to bottom for temperature, salinity, dissolved N<sub>2</sub>O and CH<sub>4</sub> concentration and saturation percent (expressed as nmol kg<sup>-1</sup> and % saturation) over the sample period.

435 **3.2. Spatial variability and annual mean regional distribution of N<sub>2</sub>O and CH<sub>4</sub> on coastal waters**  
440 **on the Mediterranean Basin scale.**

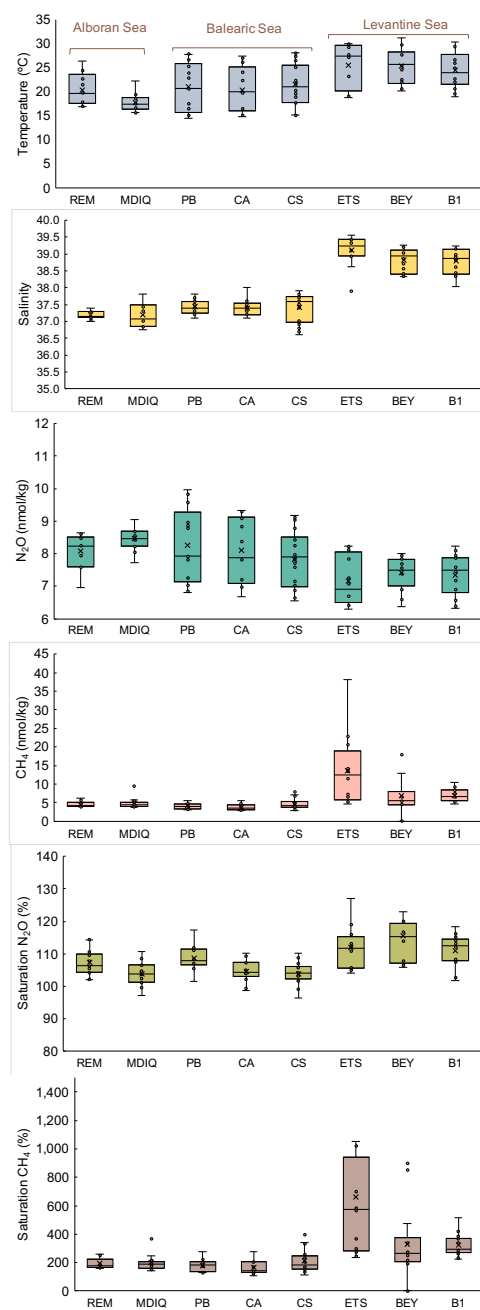
Sea Surface Temperature distribution was relatively homogeneous within each subbasin (Fig. 3) (Tukey test;  $p > 0.05$ ). However, a significant longitudinal gradient was observed across the  
440 Mediterranean Sea. The mean SST increased from  $17.7 \pm 1.8$  °C at the westernmost station (ALB-M'diq, Alboran Sea) to  $25.6 \pm 4.6$  °C at the easternmost station (LEV-ETS, Levantine Sea). Consequently, SST values were significantly higher in the Levantine Sea (B1, BEY, and ETS) compared to those in the Alboran and Balearic sub-basins (M'Diq, REM, and CA;  $p < 0.05$ ), while no significant differences were found between the latter two subbasins. A similar zonal trend was found  
445 for salinity, with mean values increasing from  $37.18 \pm 0.12$  in Alboran coastal waters to  $39.11 \pm 0.46$  in the Levantine sub-basin. This reflects a significant salinification in the Eastern basin (ETS, B1, and BEY) compared to the western Moroccan coast (M'diq, REM) and the Balearic sub-basin (CS, CA, PB), with a maximum inter-basin gradient of 1.9.

The regional distribution of CH<sub>4</sub> across the Mediterranean Sea exhibited a marked longitudinal  
450 contrast (Fig. 3). Although temporal variability was systematically higher in the eastern stations, significantly elevated mean CH<sub>4</sub> concentrations were only observed at LEV-ETS ( $13.6 \pm 9.8$  nmol kg<sup>-1</sup>; Tukey's test,  $p < 0.05$ ). In the remaining stations, average concentrations ranged from  $3.8 \pm 0.8$  nmol kg<sup>-1</sup> at BAL-CA to  $8.1 \pm 5.2$  nmol kg<sup>-1</sup> at LEV-BEY. Despite the occurrence of high episodic values at LEV-B1 and LEV-BEY, their median concentrations did not differ significantly from those  
455 in the Alboran and Balearic sub-basins (Tukey's test,  $p > 0.05$ ). Surface waters throughout the Mediterranean Sea were persistently supersaturated in CH<sub>4</sub>, with mean saturation levels ranging from  $168 \pm 46\%$  (BAL-CA) to  $659 \pm 500\%$  (LEV-ETS), following the spatial pattern of absolute concentrations. The CH<sub>4</sub>Sat oversaturation peaks along with their associated variability observed at  
460 the LEV-ETS station (up to  $659 \pm 500\%$ ) suggest the influence of localised seafloor sources, such as cold seeps or shallow gas venting, which are well documented in the Levantine sub-basin (Coleman and Ballard, 2001). Alternatively, nearshore/river filaments or submarine groundwater discharge (SGD), which can be brackish to saline and may not show as a salinity minimum, can significantly raise CH<sub>4</sub>, SST, and salinity remain mostly unchanged. In this region, the presence of coastal groundwater systems and SGD is supported by hydrogeochemical/isotopic evidence for the Mersin–  
465 Erdemli and Lamas areas (Kuyumcu, 2023). Both scenarios, seafloor sources and SGD, can likely contribute to the episodic enrichment of surface waters in this region, however further research is needed to confirm them.

In contrast, N<sub>2</sub>O concentrations showed much lower spatial variability, with station averages ranging  
470 from  $7.2 \pm 0.7$  nmol kg<sup>-1</sup> (LEV-ETS) to  $8.5 \pm 0.3$  nmol kg<sup>-1</sup> (ALB-M'DIQ) (Table 2, Fig. 3). The N<sub>2</sub>O distribution showed an inverse relationship with SST, and significant differences (Tukey,  $p < 0.05$ )

were observed only between the Eastern and Western extremes of the Mediterranean Sea. Notably,  $N_2O$  Sat levels followed an opposite longitudinal trend to absolute concentrations, with higher values at the Eastern Basin (ranging from  $100\pm 4\%$  at BAL-CS to  $116\pm 11\%$  in the Levantine stations). Despite the widespread  $N_2O$  oversaturation, these values remain relatively low compared to those in other coastal seas (Charpentier et al., 2007; Sommer et al., 2025). This finding suggests that both external inputs and in situ biological production, such as nitrification and denitrification processes in the water column or benthic compartment, are comparatively weak in coastal waters of the studied stations, consistent with the ultra-oligotrophic nature of the Mediterranean Sea.

Nutrient concentrations reflected a predominantly oligotrophic regime, although episodic enrichment was observed near the coast (Table 2). Maximum values of nitrate (up to  $7.78 \mu M$  at LEV-BEY) and phosphate (up to  $6.23 \mu M$  at LEV-B1) suggest localized continental influence. Specifically, the elevated silicate levels in the Eastern Basin (mean  $>2 \mu M$ ) coupled with high nutrient peaks point towards terrestrial runoff and potential anthropogenic inputs from major coastal urban centers as the primary drivers of coastal nutrient variability. Nutrient stoichiometry indicated a shift from the typical phosphorus-limited regime of the open Mediterranean towards nitrogen-limited conditions in several coastal sites. Specifically, low N:P ratios ( $<10$ ) in stations such as LEV-B1 and BAL-CA, coupled with high silicate concentrations (up to  $5.61 \mu mol \cdot L^{-1}$ ), suggest a strong influence of terrestrial runoff and urban effluents. This is consistent with the description of the study sites (Section 2.1), where the proximity of anthropogenic activities is identified as a potential driver of local biogeochemical variability. The highest phytoplankton biomass was recorded at LEV-BEY (mean  $0.45\pm 0.22 \mu g \cdot L^{-1}$ ), where a more balanced N:P ratio ( $\approx 18.7$ ) appears to support enhanced primary production compared to the more nitrogen-limited eastern sites.

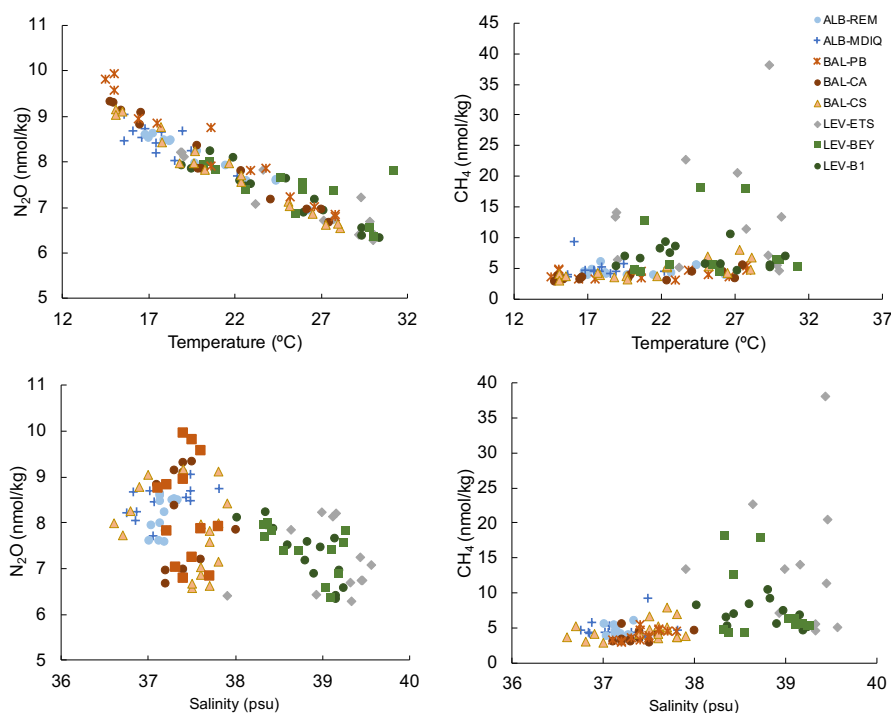


**Figure 3.** West to East spatial distribution surface temperature (°C), salinity, concentration of N<sub>2</sub>O and CH<sub>4</sub> in nmol kg<sup>-1</sup> and saturation percentage of N<sub>2</sub>O (N<sub>2</sub>OSat) and CH<sub>4</sub> (CH<sub>4</sub>Sat) across sampling stations (x-axis).

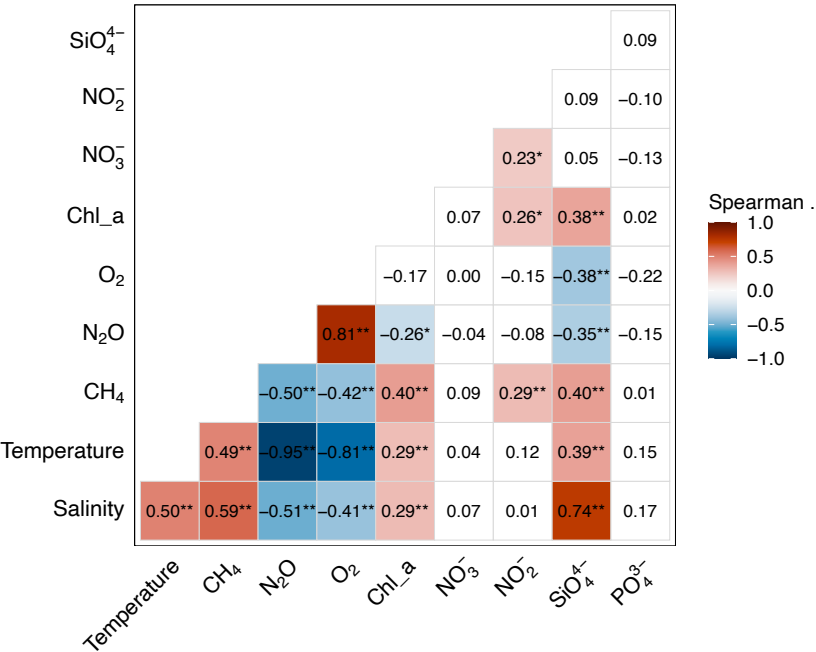
In each box-plot, the horizontal line represents the median, the cross indicates the mean, the box spans the interquartile range, and the whiskers extend to the data extremes. The listed acronyms correspond to: Ras El Ma= REM; M'diq=MDIQ; Palma Bay =PB; Cabrera =CA; Cape Salines= CS; Erdemli Time Series =ETS; Beirut=BE; Batroun =B1

### 3.3. Correlation of surface N<sub>2</sub>O and CH<sub>4</sub> with environmental variables

The N<sub>2</sub>O concentrations showed a strong negative correlation with temperature for the entire database collected from all study sites; showing that both the temporal and spatial scales of variability were highly controlled by temperature (Fig. 4). This negative correlation points to a thermodynamic control of the variability through solubility, which increases N<sub>2</sub>O in colder water. However, there was a positive correlation between N<sub>2</sub>OSat and temperature ( $N_2OSat = 0.82 \cdot T + 89.96$ ;  $r = 0.58$ ,  $n = 109$ ,  $p < 0.01$ ), with higher values in summer in the Eastern Basin than in winter in the Western Basin, corresponding to an enhancement of N<sub>2</sub>O microbial production with increasing temperature. In contrast, CH<sub>4</sub> concentrations showed the opposite behaviour to N<sub>2</sub>O, with greater variability and a positive correlation with temperature, indicating mechanisms other than solubility controlling the variability and important sources of CH<sub>4</sub> in the Eastern Basin.



515 **Figure 4.** Scatter plots illustrating the relationship between dissolved N<sub>2</sub>O and CH<sub>4</sub> concentrations (nmol kg<sup>-1</sup>) and key environmental variables: surface water temperature (°C) and salinity. Data from all stations are included, highlighting the overall trends across the Mediterranean Basin



520 **Figure 5.** Spearman's rank correlation matrix showing the interrelationships between N<sub>2</sub>O and CH<sub>4</sub> concentrations and various environmental parameters (temperature, salinity, dissolved oxygen, nutrients, chlorophyll a) for the entire dataset, excluding data from LEV-ETS due to missing ancillary variables. Significant correlations are indicated with asterisk (\*\*:  $p < 0.01$ ; \*:  $p < 0.05$ ).

525 The Spearman correlation matrix accounts for overall variability at both temporal and spatial scales, as shown in Fig. 5 for N<sub>2</sub>O and CH<sub>4</sub> concentrations. The correlation analysis showed that N<sub>2</sub>O was strongly correlated with temperature ( $-0.95$ ,  $p < 0.01$ ) and significantly negatively correlated with salinity ( $-0.51$ ,  $p < 0.01$ ), Chl a ( $-0.26$ ,  $p < 0.05$ ), and silicate ( $-0.35$ ). ( $p < 0.01$ ) and was highly positively correlated with O<sub>2</sub> ( $r = 0.81$ ,  $p < 0.01$ ). The CH<sub>4</sub> showed an opposite behaviour, with a significant negative correlation with oxygen ( $-0.42$ ,  $p < 0.01$ ) and positive correlation with salinity ( $r = 0.59$ ,  $p < 0.01$ ), temperature ( $0.49$ ,  $p < 0.01$ ), Chl a ( $0.4$ ,  $p < 0.01$ ), and silicate ( $0.4$ ,  $p < 0.01$ ).  
530 Temperature was clearly the main controlling factor, especially for N<sub>2</sub>O, and the overall correlation with salinity was stronger than when the analysis was performed at every station. This could be due to the higher salinity in the Levantine Sea and the zonal distribution pattern of salinity in the basin  
535 itself. Furthermore, the analysis of the Spearman correlation matrix for each station revealed additional local mechanisms acting on the seasonal scale that could be relevant, such as a significant

positive correlation in O<sub>2</sub> among Western Mediterranean stations (BAL-CA, BAL-CS, BAL-PB, and BAL-REM) that was not significant in the eastern Levantine sub-basin. In addition, the strong negative correlation between N<sub>2</sub>O and temperature was ubiquitous across stations but was only correlated with salinity in LEV-B1 (negative correlation) and ALB-M'DIQ (positive correlation). Finally, Chl *a* was only significant for temporal variability at the LEV-BEY and BAL-CS stations. Although oceanic CH<sub>4</sub> often exhibits a strong depth dependence (Weber et al., 2019), station depth was included in our initial correlation matrix but yielded no significant relationship ( $p > 0.05$ ). This lack of correlation indicates that CH<sub>4</sub> variability found among stations in our study in our study area is primarily driven by other sedimentary sources rather than depth-dependent benthic remineralization.

Our study is consistent with previous studies in the Eastern (Bange et al., 1996) and Western Mediterranean Sea (de la Paz et al., 2015, Flecha et al., 2023, 2025), where temperature was revealed to be the main controlling factor of surface N<sub>2</sub>O and CH<sub>4</sub> variability.

#### 3.4 Air-sea fluxes of N<sub>2</sub>O and CH<sub>4</sub>

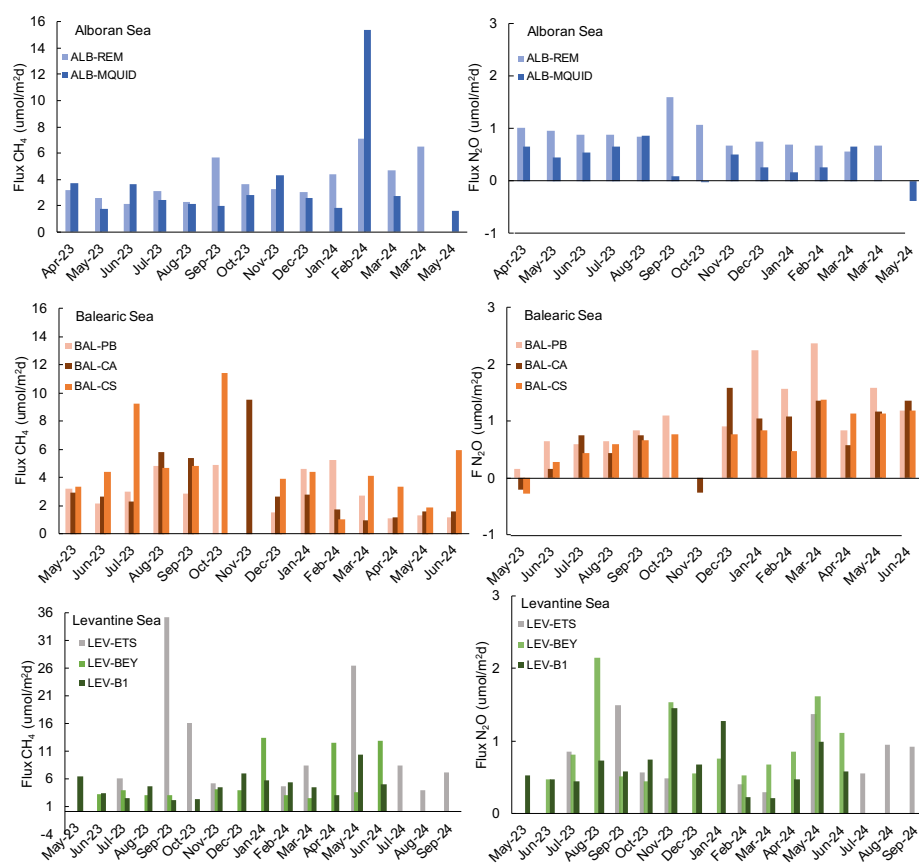
Surface waters were consistently supersaturated with CH<sub>4</sub> relative to the atmosphere at all the coastal Mediterranean stations (Table 2). Consequently, the region acted as a net CH<sub>4</sub> source, with air-sea flux exhibiting high temporal variability (Table 3). Fluxes ranged from 0.97 to 11.41  $\mu\text{mol m}^{-2} \text{d}^{-1}$  in the Balearic sub-basin, 1.74 to 15.4  $\mu\text{mol m}^{-2} \text{d}^{-1}$  in the Alboran sub-basin, and reached a maximum of 35.2  $\mu\text{mol m}^{-2} \text{d}^{-1}$  in the Levantine Sea (Fig. 6, Table 2). While no uniform seasonal trend was observed basin-wide, a notable regional decoupling occurred: maximum CH<sub>4</sub> outgassing in the Balearic sub-basin (July–November 2023) coincided with the lowest flux periods in the Alboran and Levantine sub-basins.

In contrast, N<sub>2</sub>OSat and subsequent air-sea exchange followed a more distinct seasonal trend. Most stations remained moderately supersaturated, acting as a minor N<sub>2</sub>O source, with the exception of brief undersaturation events (>98%) in the Balearic sub-basin in May and November 2023. N<sub>2</sub>O fluxes peaked in the Balearic sub-basin at 2.37  $\mu\text{mol m}^{-2} \text{d}^{-1}$  (January 2024), driven by a combination of supersaturation and intensified winter wind speeds in the Western Mediterranean. Overall, the N<sub>2</sub>O flux variability mirrored seasonal concentration changes but was strongly modulated by wind-driven gas transfer.

The annual flux average (Table 3) confirmed that all stations behaved as net annual sources of both CH<sub>4</sub> and N<sub>2</sub>O. The highest mean CH<sub>4</sub> fluxes were recorded at the Erdemli site (LEV-ETS: 13.68±9.57  $\mu\text{mol m}^{-2} \text{d}^{-1}$ ). At this site, the substantial discrepancy between the mean and median (8.39  $\mu\text{mol m}^{-2} \text{d}^{-1}$ ) highlights a heavily right-skewed distribution caused by episodically high-concentration events unique to the Levantine Sea. Conversely, annual N<sub>2</sub>O fluxes were remarkably homogeneous

575 across subbasins, ranging from  $0.42 \pm 0.26 \mu\text{mol m}^{-2} \text{d}^{-1}$  (ALB-M'DIQ) to  $1.11 \pm 0.64 \mu\text{mol m}^{-2} \text{d}^{-1}$   
(BAL-PB), showing a symmetric distribution with closely aligned mean and median values.

580 The magnitude of the air-sea fluxes calculated in this study is consistent with the sparse literature  
on the Mediterranean Sea. Our  $\text{CH}_4$  fluxes in the Alboran sub-basin ( $1.74$  to  $15.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ )  
aligned with the ranges reported by de la Paz et al. (2015) in the Strait of Gibraltar and the recent  
observations by Flecha et al. (2023, 2025), who highlighted the coastal Alboran and Balearic seas  
as persistent sources of  $\text{CH}_4$  emissions. The annual mean fluxes of  $\text{N}_2\text{O}$  ( $0.42$  to  $1.11 \mu\text{mol m}^{-2} \text{d}^{-1}$ )  
are in excellent agreement with the values reported by Bange et al. (1996) for the Aegean Sea ( $0.1$   
to  $1.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ ), confirming that both the Eastern and Western basins act as moderate but steady  
585 sources of  $\text{N}_2\text{O}$  to the atmosphere. However, the episodic high-flux events recorded at the LEV-ETS  
station represent some of the highest  $\text{CH}_4$  emission rates documented for the offshore Levantine  
sub-basin, emphasising the role of localised coastal hotspots in the regional greenhouse gas budget.



**Figure 6.** Time-series of air-sea fluxes of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  in  $\text{nmol m}^{-2} \text{d}^{-1}$  for each station, shown by marine ecoregions.

600 **Table 3.** Range (min-max) of air-sea fluxes for each station, and median and average annual N<sub>2</sub>O and CH<sub>4</sub> air-sea flux (μmol m<sup>-2</sup> d<sup>-1</sup>) calculated using the expression for gas exchange rate proposed by Wanninkhof (2014).

|               | Site<br>Station<br>Code | F CH <sub>4</sub> (μmol m <sup>-2</sup> d <sup>-1</sup> ) |        |            | F N <sub>2</sub> O (μmol m <sup>-2</sup> d <sup>-1</sup> ) |        |           |
|---------------|-------------------------|-----------------------------------------------------------|--------|------------|------------------------------------------------------------|--------|-----------|
|               |                         | Range                                                     | Median | Mean ± SD  | Range                                                      | Median | Mean ± SD |
| Balearic Sea  | BAL-CA                  | 1-9.6                                                     | 2.73   | 3.80±2.59  | -0.25-1.58                                                 | 0.75   | 0.67±0.55 |
|               | BAL-CS                  | 1-11.4                                                    | 4.40   | 5.46±3.09  | -0.27-1.37                                                 | 0.71   | 0.68±0.42 |
|               | BAL-PB                  | 1.1-5.2                                                   | 3.10   | 3.36±1.23  | 0.16-2.37                                                  | 0.87   | 1.11±0.64 |
| Levantine Sea | LEV-B1                  | 2.1-10.3                                                  | 4.47   | 4.57±2.23  | 0.21-1.45                                                  | 0.63   | 0.69±0.69 |
|               | LEV-BEY                 | 2.5-13.4                                                  | 3.60   | 4.99±3.59  | 0.47-2.15                                                  | 0.78   | 0.95±0.51 |
|               | LEV-ETS                 | 4.5-35.2                                                  | 8.39   | 13.68±9.57 | 0.3-1.49                                                   | 0.65   | 0.79±0.39 |
| Alboran Sea   | ALB-M'DIQ               | 1.7-15.4                                                  | 2.67   | 3.79±3.59  | -0.03-0.86                                                 | 0.48   | 0.42±0.26 |
|               | ALB-REM                 | 2.1-7.1                                                   | 3.26   | 3.77±1.41  | 0.56-1.58                                                  | 0.86   | 0.88±0.26 |

605 **Table 4.** Annual aaverage N<sub>2</sub>O and CH<sub>4</sub> air-sea flux (μmol m<sup>-2</sup> d<sup>-1</sup>) for this study and other data published data in the Mediterranean Sea. \* For the Strait of Gibraltar, the range of observed CH<sub>4</sub> values is presented instead of a mean due to incomplete seasonal coverage in the original study.

| Region              | Reference               | Flux CH <sub>4</sub> (μmol m <sup>-2</sup> d <sup>-1</sup> ) | Flux N <sub>2</sub> O (μmol m <sup>-2</sup> d <sup>-1</sup> ) |
|---------------------|-------------------------|--------------------------------------------------------------|---------------------------------------------------------------|
| Strait of Gibraltar | de la Paz et al. (2015) | 0 - 1.68 *                                                   | 0.35±0.27                                                     |
| Balearic Sea        | Flecha et al. (2023/25) | ~0.2 - 9.7 (1.4±1.4)                                         | -0.3-0.6 (0.1±0.2)                                            |
| Aegean Sea          | Bange et al. (1996)     | 0.26-14.5 (mean 1.7)                                         | 0.1 - 1.7                                                     |
| Alboran Sea         | This study              | 3.8 ±3.6                                                     | 0.9 ±3                                                        |
| Balearic Sea        | This study              | 4.2 ±1.3                                                     | 0.8±0.5                                                       |
| Levantine Sea       | This study              | 7.7±5.1                                                      | 0.8±0.5                                                       |

**4. Data availability**

Data described in this paper are accessible at the Zenodo repository <https://doi.org/10.5281/zenodo.19351642> (de la Paz et al.,2026).

Deleted: <https://doi.org/10.5281/zenodo.19351642> (de la Paz et al.,2026). During the peer-review process, anonymous access is restricted via DOI until publication; however, data are available upon email request to the corresponding author for other interested parties

## 6. Conclusions

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This data paper presents the first comprehensive, seasonally-resolved dataset of N<sub>2</sub>O and CH<sub>4</sub> concentrations and air-sea fluxes across under-sampled coastal regions of the Mediterranean Sea. Our results confirm that these coastal waters consistently act as a net source of both N<sub>2</sub>O and CH<sub>4</sub> to the atmosphere. We found a strong thermodynamic control on N<sub>2</sub>O variability, with higher concentrations in colder waters and moderate oversaturation throughout the Mediterranean Sea. In contrast, CH<sub>4</sub> dynamics were highly variable, positively correlated with temperature, and marked by episodic high-flux events, particularly in the Levantine Sea, indicating the influence of localized geological or anthropogenic sources. Despite challenges in assessing changes in N<sub>2</sub>O and CH<sub>4</sub> in coastal water due to limited measurements, this dataset contributes to the understanding of greenhouse gas variability in the region. This quality-controlled ROADSTER dataset provides a valuable regional resource that enables accurate trend quantification and change estimation, serving as an essential baseline for evaluating environmental impacts, refining regional non-CO<sub>2</sub> greenhouse gas budgets, and improving global climate models.

## 11. Author contribution

MdIP conducted the sample analyses, performed the data analyses, and wrote the first draft of the manuscript. SF, FB, MF, VI, KÖ, and IEH collected samples. SF, MdP and AERH contributed to the design of the study. FFP contributed to data analysis. IEH designed and led the study. All authors contributed to discussions on sample design and collection and data analysis, and reviewed, revised, and approved the final version of the manuscript.

## 12. Competing interests

The contact author has declared that none of the authors has any competing interests

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