An update on dissolved methane distribution in the North subtropical Atlantic Ocean

Anna Kolomijeca[1,2] Lukas Marx[3], Sarah Reynolds[3], Thierry Cariou[1,4], Edward Mawji[5], Cedric Boulart[1]

[1] UMR 7144 CNRS Sorbonne Université, Station Biologique de Roscoff, 29680 Roscoff, France
[2] MARUM, Center for Marine Environmental Sciences, D-28359 Bremen, Germany
[3] School of the Environment, Geography and Geosciences, University of Portsmouth, PO1 2UP Portsmouth, UK
[4] IRD, UAR191, Instrumentation, Moyens Analytiques, Observatoires en Géophysique et Océanographie (IMAGO), Technopôle de Brest-Iroise, 29280 Plouzané, France
[5] National Oceanography Centre, European Way, Southampton, SO14 3ZH, UK

Correspondence to: Anna Kolomijeca (akolomijeca@marum.de)

Abstract. Methane (CH_4) is a potent greenhouse gas and plays a significant role in recent increasing global temperatures. The oceans are a natural source of methane contributing to atmospheric methane concentrations, yet our understanding of the oceanic methane cycle is poorly constrained. ~~is the second most produced greenhouse gas after carbon dioxide, but~~however ~~the role of the open ocean in~~ on its natural cycle ~~remains poorly constrained~~understood. ~~~~Accumulating evidence indicates that a significant part of oceanic CH_4 is produced in oxygenated surface waters as a by-product of phytoplanktonic activity. This study focussed on t~~The subtropical North Atlantic Ocean ~~(between~~ 26ºN 80'W and 26ºN 18'W) ~~was investigated for the~~where the distribution of dissolved CH_4 concentrations and associated air-sea fluxes during winter 2020 were investigated. Water samples from 64 stations were collected from the upper water column up to depths of 400 m. The upper oxic mixed-layer was oversaturated in dissolved CH_4 with concentrations ranging between 3-7 nmol/l ~~and~~ with the ~~, with the highest~~highest ~~values~~ concentrations of 7-10 nmol/l found to the east of the transect, consistent with other subtropical regions of the world's oceans. The high anomalies of dissolved CH_4 ~~appeared to be~~were found to be ~~associated to~~ with phosphate~~orus~~ depleted waters and regions where the abundance of the ubiquitous pico-cyanobacteria, *Synechococcus* and *Prochlorococcus* were elevated. ~~to a peak of regions of elevated phytoplankton abundance. Further investigations indicated a correlation between CH_4 anomalies, phosphate depletion and the abundance of two ubiquitous pico-cyanobacteria, *Synechococcus* and *Prochlorococcus*.~~ ~~A~~although other phytoplanktonic phyla cannot be excluded~~, both appeared to~~this suggest that cyanobacteria ~~substantially contribute to the ocean methane paradox~~contribute to the release of CH_4 in this region.~~.~~ The calculation of air-sea fluxes further confirm~~eds~~ that the subtropical North Atlantic Ocean as a source of CH_4. ~~, mainly produced by phytoplanktonic activity in surface waters.~~This study provides evidence to corroborate the key role that pico-cyanobacteria play in helping to explain the oversaturation of CH_4 found in surface mixed layer of the open ocean, otherwise known as the 'Ocean Methane Paradox'.

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1. Introduction

Since the industrial revolution, the average global temperature has increased at the fastest rate in recorded history, primarily driven by growing emissions of greenhouse gases (GHGs). Among them, methane (CH_4) is considered the second largest contributor to Earth warming, after carbon dioxide (CO_2), with an atmospheric concentration of 1,866 ppb (IPCC, 2021). Over the last 50 years, CH_4 concentrations have increased by 20 % ~~(Karl et al., 2008),~~ (Karl et al., 2008; ~~(~~Rhee et al., 2009) – and ~~is~~ are expected to rise further, by approximately 2 % per year (Dang and Li, 2018).

Oceans ~~are~~ were generally ~~thought~~ considered ~~of as a~~to be a minor contributor to the total global CH_4 budget, ~~however,~~yet recent calculations indicate that oceans could emit 6 to 17 Tg CH_4/yr, i.e. 1 to 10 % of the total natural emissions (Weber et al., 2019). This large variability reflects the great uncertainty on the contribution of natural sources due to a lack of data and understanding of the sources and controls on oceanic CH_4 emissions. ~~, when compared to carbon dioxide (CO_2). CH_4 is traditionally thought to be produced by microbial anaerobic methanogenesis in marine sediments as a consequence of the degradation of organic matter; it accumulates in the sediment, eventually forming gas hydrates, which may then be released into the water column. Under the influence of pressure and temperature CH_4 diffuses out of the sediment and ebullition carries CH_4 to the atmosphere (Weber et al., 2019).~~

The marine flux of CH_4 results from the balance between production and oxidation processes, as for instance, the microbial anaerobic oxidation of CH_4 (AOM) in sediments significantly decreases CH_4 fluxes to the atmosphere, thus representing an important carbon sink in the ocean (Oppo et al., 2020). In fact, the marine flux is dominated by shallow coastal environments including estuaries (up to 75 % (Weber et al., 2019). In marine sediments CH_4 can be released via microbial anaerobic methanogenesis as a consequence of the degradation of organic matter; it accumulates in the sediment, eventually forming gas hydrates, which may then be released into the overlying water column. Under the influence of pressure and temperature CH_4 diffuses out of the sediment and ebullition carries CH_4 to the atmosphere (Weber et al., 2019).

In the open oxygenated waters, the primary mechanism controlling the CH_4 emissions is aerobic methanotrophy that converts CH_4 into CO_2 (Weber et al., 2019). However, this process ~~may~~ could be overcome by *in-situ* production of CH_4 in upper oxic waters that can significantly contribute to marine CH_4 fluxes to the atmosphere. Typical CH_4 depth distribution in the open ocean indicates a general oversaturation in the mixed layer (Reeburgh, 2007a)~~.~~; In the surface waters of the Pacific Ocean (Weller et al., 2013), the Indian Ocean (Bui et al., 2018) and the Atlantic Ocean, values of 2-5 nmol/l and a maximum of 10 nmol/l were measured near the surface (Scranton and Brewer, 1977). These observations make the global ocean a net source of CH_4 ~~for~~ to the atmosphere with a weighted supersaturation of 120 % (Kock and Bange, 2007). Exemptions are the Southern Ocean and the central Arctic Ocean, where surface waters are undersaturated in CH_4, either due to extensive upwelling supplying CH_4-depleted water to the surface (Bui et al., 2018), or the limitation of air-sea exchanges by ice cover (Weber et al., 2019).

The oversaturation of the surface mixed layer, commonly known as the "ocean methane paradox" (OMP), was ~~initially described~~explained ~~as~~ by ~~a~~ the result of ~~the~~ methanogenic activity from *Archaea* living within anaerobic cavities of ~~the~~

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zooplankton guts and anaerobic micor-environments inside sinking particles of organic matter (Reeburgh, 2007a). Initially, only microbes from the *Archaea* domain were thought to have the capability ies of producing CH_4 under strict anaerobic conditions. Although one cannot exclude this process to explain the methane paradox (Schmale et al., 2018) (Stawiarski et al., 2019), an increasing number of studies focus have revealed on the relationships between CH_4 anomalies in surface waters and the presence of certain phytoplanktonic groups such as coccolithophores (Lenhart et al., 2016a) or and cyanobacteria (Bižić et al., 2020).

Cyanobacteria are ubiquitous to every aqueous environment on Earth, both in illuminated and dark water bodies (Percival and Williams, 2013). In the open ocean, small-sized picophytoplankton of the genera *Prochlorococcus spp.* and *Synechococcus spp.* account for ~80 % of the total phytoplanktonic chlorophyll *a* (Hickman et al., 2010) and could represent up to 8.5 and 16.7 % of the ocean net primary production (ONPP), respectively (Flombaum et al., 2013). Generally, nutrient limitation sets the upper limit for primary production and the distribution of *Prochlorococcus* and *Synechococcus*; The oligotrophic subtropical North Atlantic in fact is nitrogen (N) - phosphorus (P) co-limited (Harvey et al., 2013), hence cyanobacteria need to acquire these nutrients from alternative sources. New nitrogen to the surface ocean is introduced via Whereas bbiological nitrogen fixation by diazotrophs which can supplylies upto globally 163.2 Tg new nitrogen per year globally (Wang et al., 2019). With regard to P,- *Prochlorococcus* and *Synechococcus* mostly depend on the remineralisation of dissolved organic phosphorus (DOP) via hydrolytic enzymes (e.g. alkaline phosphatase (Muñoz-Marín et al., 2020))). Additionally, evidence is mounting that cyanobacteria are major sources of semi-labile dissolved organic matter (DOM) phosphonates (Repeta et al., 2016). The bacterial degradation of methylphosphonates (MPn) releases CH_4 and therefore cyanobacteria might are thought to play a key role in the global marine CH_4 flux. Laboratory-based studies with *Prochlorococcus* and *Synechococcus* confirmed a substantial production of CH_4 of up to 0.51 ± 0.26 μmol g^{-1} $hour^{-1}$ (Bižić et al., 2020).

However, *in-situ* production of CH_4 is difficult to assess, due to the complexity of biogeochemical and physical processes involved in the marine CH_4 flux. Additionally, nutrient availability impacts the metabolic pathways of the cyanobacterial community.

CH_4 *I*i*n-situ* production of CH_4 results is a repercussion from different metabolic pathways including the conversion of methylated substrates, which and are induced by environmental stress (e.g. nutrient supplyies, temperature variations, light and variations in temperature, salinity and light attenuation). As such, CH_4 may be the by-product of the methylphosphonate decomposition remineralisation in phosphate-stressed surface waters, i.e. the MPn way (Karl et al., 2008, Bizic et al 2020). Due to the strong depletion of inorganic phosphorus in some oligotrophic areas in the Atlantic or the Pacific Oceans, cyanobacteria use the organic phosphonates as a P source (Feingersch et al., 2012), leading to the release of methyl groups in the water that are rapidly converted into CH_4 (Beversdorf et al., 2010).

In contrast, nitrate availability might control CH_4 production in phosphate replete surface waters. While in P-limited waters cyanobacteria use methylphosphonate as a nutrient source and hence release CH_4, in N-limited waters, CH_4 may result from the breakdown of DMSP (dDiy-methylsulffoniopropionate) into DMS (Dimethyl Sulfide) by bacteria as they use DMSP as a

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C source (Florez-Leiva et al., 2013). Other environmental parameters, such as variations in temperature or light attenuation may also influence CH_4 formation, although data is lacking to fully understand the metabolic pathways leading to CH_4 production.

In the current context of climate change and ~~resulting consequences to the marine environment~~warming ocean waters, we are likely to expect a shift in the community of primary producers towards smaller sized cyanobacteria such as *Prochlorococcus* and *Synechococcus* (van de Waal and Litchman, 2020), with a concurrent decrease in total biomass in the open ocean (Marinov et al., 2010). Yet, with accumulating evidence ~~of~~ on the importance of the cyanobacterial contribution towards CH_4 production and given the important role of CH_4 as a potent GHG, it is crucial to intensify the monitoring and investigating of CH_4 production and fluxes in surface oceanic waters in order to feed a global database (Bange et al., 2009). There is a lack of data to comprehend the current and future role of the ~~the~~ Earth's oceans and primary production ~~within these in~~ in relation to the global CH_4 budget.

In the present paper, we provide an update on the dissolved CH_4 concentrations and air-sea fluxes of CH_4 in surface waters of the subtropical North Atlantic Ocean as part of the JC191 hydrographical cruise (RRS James Cook, Jan-Mar 2020). Furthermore, we present data of the distribution of the two dominant cyanobacteria, *Prochlorococcus* and *Synechococcus* to highlight the contribution of the planktonic community to the CH_4 flux. More specifically, our objectives were to confirm the presence of CH_4 anomalies in surface waters and the associated air-sea fluxes, and to propose possible mechanisms and sources controlling the CH_4 distribution by examining the relationships between ~~the~~ physico-chemical and ~~the~~ biological parameters.

2. Methods

2.1 Water sampling and analysis for dissolved gas concentrations

Seawater samples were collected during the JC191 hydrographical cruise (as part of the GO-SHIP program, PI A. Sanchez-Franks (Sanchez-franks, 2020)) on board the RRS James Cook between January-March 2020 along a west-east transect in the subtropical North Atlantic from Fort Lauderdale, USA to Santa Cruz de Tenerife, Spain on the nominal 24°N parallel. 64 profiles (out of 135 stations occupied by CTD casts in total) from surface to 400 m depth (or full-depth for the shallower continental margin stations) were sampled (Figure~~.~~ 1).

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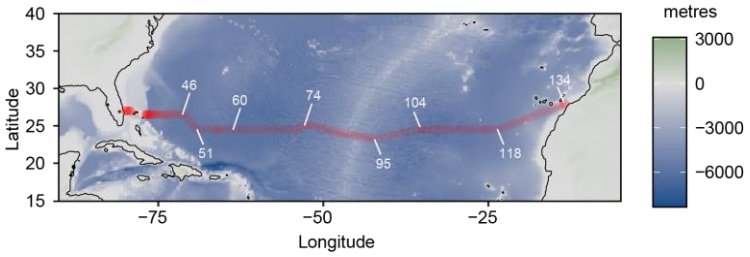

Figure 1. Cruise track of JC191 24N expedition from Fort Lauderdale, USA to Santa Cruz de Tenerife, Spain (January – March 2020). White numbers indicates some of the total 135 CTD stations.

Water samples for dissolved CH_4 measurements were collected into 20-ml headspace vials using a 24-Niskin Bottle rosette equipped with a SBE911+ CTD (Conductivity, Temperature, Depth), a AquaTracka III fluorometer (Chelsea Technologies) and a dDissolved oOxygen Sensor (Seabird SBE 43). Dissolved gas samples were poisoned with $Hg(Cl)_2$, then fitted with Teflon stopcocks and crimp-sealed under exclusion of any air bubbles. Immediately after sampling, Ssamples were immediately stored at 4 °C after sampling until analysis on shore at the Station Biologique de Roscoff.

Gas extraction and analyses were performed using a Shimadzu Headspace Sampler (HS-20) connected to a gas chromatograph (Shimadzu GC-2030), fitted with a barrier discharge ionization detector (BID) and a 30-m SH-Rt-MSieve 5A column. With this set-up, headspace extraction is entirely automated with pressurization of the sample up to 2 bars, heating at 90 °C and equilibration for 7 minutes. An aliquot of the gas sample was transferred to a 1-ml injection loop, maintained at 150 °C and injected into a 50 °C heated column. Calibrations were made by injecting known volume of standard gas (Messer®, 1000 ppm, 500 ppm and 100 ppm (-+ 1ppm), CH_4 in helium and 500 ppb H_2 in helium). All analyses were made in duplicate and results are given as averaged values. The detection threshold of this method is 0.2 nmol for dissolved CH_4 and variation between duplicates was 5%.

2.2 Inorganic Nutrient Analysis

Samples for inorganic nutrient analysis (NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}) were collected unfiltered into sterile 15 ml centrifuge tubes (rinsed three times with water from the same Niskin). Samples were analysed directly from the collection tubes within 1-8 hours and measured from the lowest to the highest concentration (surface to deep) to reduce any carry over effects. Nutrients were analysed on board using a 4-channel Seal Analytical AA3 segmented flow autoanalyzer following GO-SHIP protocols (Becker et al., 2020).)

In order to test the accuracy and precision of the analyses, certified reference materials (CRMs) from KANSO Technos Co. (lots lot CD, CJ, CI and lot BW) were measured in triplicate in every run.

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2.3 Cyanobacteria sampling and analysis

38 of the stations occupied during JC-191 were sampled at six depths in the upper water column (max. sampling depth 375 m) following the live fluorescence profiles ~~(AquaTracka III, Chelsea Technologies)~~, to determine the prevailing community of primary producers (unpublished data, Marx 2020). Bulk water samples (5 L) were collected from Niskin bottles, from which then subsamples for the flow cytometric determination of *Prochlorococcus* and *Synechococcus* abundances were collected. 4 ml of sample water were immediately fixed with 40 µl Glutaraldehyde solution (50%) and stored at 4°C until transferred to a low temperature freezer (-80 °C) after 12 hours.

Samples were analysed at the University of Portsmouth on a CyFlow Cube 8 (Sysmex) flow cytometer immediately after defrosting and at a flowrate of 1 µl/s. The distinction between *Prochlorococcus* and *Synechococcus* was achieved by gating each group according to its fluorescence signals (red and orange fluorescence) against the size fractionation (forward and side scatter). For each of the stations sampled, the mixed layer depth (MLD, defined as the depth at which temperature decreased by 1 °C from the surface) was determined and the integrated average in abundance above said MLD was calculated.

2.4 Statistical analyses

In order to determine the biological and physico-chemical parameters that influence the distribution of dissolved methane in surface waters, a principal component analysis (PCA) was applied. This statistical tool simplifies the underlying structure of the multivariate dataset, converting a large number of variables into a smaller number of variables, i.e. components (PCs) with a minimum loss of information. Each PC is ~~usually~~ associated to an eigenvalue that indicates the variation in the data. ~~Here, t~~Here, the PCA computes a singular value decomposition of the data matrix and does not incorporate eigenvalue of the covariance matrix to maintain numerical accuracy. Then, factor loadings were calculated, where a high factor loading indicates a significant correlation between variables. Additionally, Kendall rank correlations were computed to evaluate associations between two variables (e.g. methane concentrations and fluorescence or phytoplankton abundances). All statistics were performed with RStudio and the R 'stats' package' (Foundation for Statistical Computing, Vienna, 2013).

~~was performed using RStudio and the R 'stats' package' (Foundation for Statistical Computing, Vienna, 2013), in which the calculation is done by a singular value decomposition of the data matrix, not by using eigen on the covariance matrix. This method is preferred for numerical accuracy. Factor loadings were then calculated: high factor loadings indicate significant correlation between variables.~~

~~In addition to the PCA, we ran simple correlation tests to evaluate the association between two variables (e.g. methane concentrations and fluorescence or phytoplankton abundances) for some stations. We used here the Kendall rank correlation coefficient as the data do not follow a bivariate normal distribution according to the Shapiro-Wilk test.~~

2.5 Flux calculation

The flux of air-sea CH_4 was calculated following established methods based on (Kelley and Jeffrey, 2002a; Wanninkhof, 2014)

$$F = k (C_w – C_a)$$

Where~~,~~ F is the CH_4 flux (mol m^{-2} d^{-1}) from sea-water to air, with k as gas transfer coefficient under consideration of wind speed, C_w as average CH_4 concentration measured in surface water and C_a as equilibrated seawater-air CH_4 concentration. ~~; k – gas transfer coefficient, related to wind speed; C_w – average measured CH_4 concentration in the surface water, and C_a – air-balancing (equilibrated) sea water CH_4 concentration. The w~~Wind speed data w~~as~~ere obtained ~~during the cruise~~from on-ship measurements throughout the cruise transect and concentration of CH_4 ~~concentration~~ in the air was assumed to be 1.9 ppm (based on NOAA, Global Monitoring Laboratory https://www.esrl.noaa.gov report).

The ~~G~~gas transfer coefficient k~~,~~ was calculated ~~based on the relationship provided by~~following ~~(Wanninkhof, 2014):~~:

$$k = 0.251 <U^2> (Sc/660)^{-.05}$$

where $<U^2>$ represents the average of neutral stability of winds at 10 m height squared and Sc indicated the Schmidt number, taking into account the kinematic viscosity of water and the molecular diffusion coefficient of the gas. From inverse modelling using CCMP winds and the Modular Ocean Model – General Circulation model (MOM3 GCM), a value of 0.251 was obtained. Sc was calculated as ~~Where, the value of 0.25 1 is obtained from inverse modelling approach, the CCMP winds, and the Modular Ocean Model General Circulation model, MOM3 GCM, as proposed by (Wanninkhof, 2014); <U2> is average of neutral stability winds at 10 m height squared, or the second moment. Sc is Schmidt number, which is kinematic viscosity of the water divided by the molecular diffusion coefficient of the gas.~~

~~Sc was calculated as~~ $Sc = A + Bt + Ct^2 + dt^3 + Et^4$

with coefficients A, B, C, D and E obtained from a least square fourth-order polynomial fit

~~Coefficients (A, B, C, D and E) for a least squares fourth-order polynomial fit were obtained from~~ (Wanninkhof, 2014).

3. Results

3.1 Spatial distribution of physico-chemical parameters

CH_4 concentrations in surface waters of the subtropical North Atlantic ~~ocean~~ along the 24°ranset~~parallel~~ t were distributed non-uniformly between 3-10 nmol/l, i.e. systematically above saturation of ~2.7 nmol/l. Lowest concentrations of CH_4 of 3-4 nmol/l were found in the central gyre system above the mid-Atlantic ridge (~ 45 °W), with increasing values of 8-10 nmol/l in both western and eastern boundaries closer to the continental shelf (Figure 2a).

Chlorophyll *a* (~~Figure 2b,~~ Chl *a*, Figure 2b) from real-time fluorescence profiles~~,~~ exhibit highest concentrations near both western and eastern shore systems~~, with~~ and lowest concentrations in surface waters throughout the central gyre system (< 0.1 µg/l, Figure 2). ~~Nonetheless,~~A deep chlorophyll maxima (DCM) was observed between 100-130 m water depth and was consistently above the mixed layer depth (MLD). ~~were observed sitting right above MLD at ~ 100-130 m water depth.~~ Concentrations of Chl *a* increase towards the Mauritanian upwelling off the North African coast to above 0.4 µg/l, indicating higher primary production due to enhanced nutrient supply. Accordingly, light transmission is decreased due to higher content of suspended particles in the water column (Figure 2h). Furthermore, fluorescence does align with patterns of dissolved oxygen in the water column of this transect. The surface waters in the subtropical North Atlantic are well oxygenated with concentrations above 200 µmol/kg in the top 100 metres of the water column, subsequently decreasing with depth. ~~Also, i~~Increased concentrations of dissolved oxygen are observed towards the eastern boundary following enhanced lateral transport from the coastal upwelling (Figure 2e).

~~Phosphate~~ Nitrate and phosphate~~nitrate~~ concentrations were low (< 0.1 µmol/kg, <0.01 µmol/kg, respectively) in surface waters throughout the transect with nutriclines >200 m depth, shallowing (<150 m in eastern basin and <100 m in eastern boundary) towards the eastern boundary due to coastal upwelling off the eastern North African coast and associated enhanced mixing of deep, nutrient enriched waters into surface waters (Figure 2c and d).

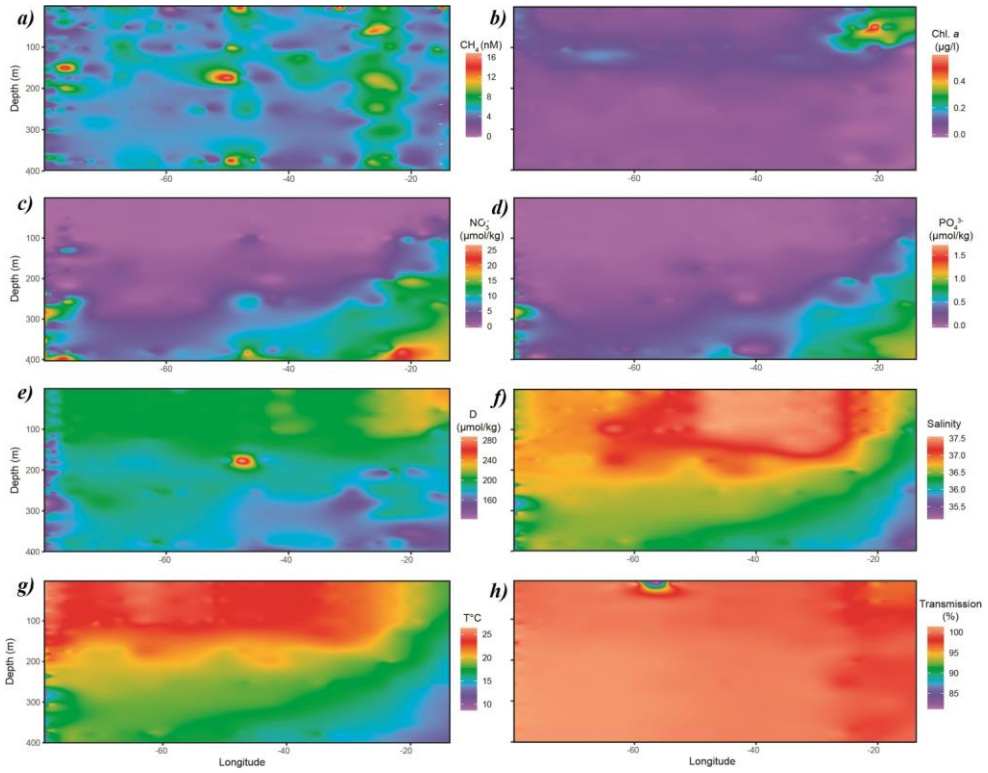

Figure 2. Distribution of a) CH_4, b) Chl *a*, c) NO_3, d) PO_4, e) dissolved oxygen, f) salinity, g) temperature and h) transmission along the cruise track. Chl *a*, dissolved oxygen, salinity, temperature and transmission data originate from sensors of and attached to the CTD. CH_4, NO_3 and PO_4 were measured analytically. Part of the data were taken from CCHDO (Sanchez-franks, 2020).

3.2 Sea-to-air methane flux

At most stations, air-sea CH_4 flux was 1-2 µmol m^{-2} d^{-1}, with maximum values of 5 µmol m^{-2} d^{-1} in the area of 24 °N 25 °W (Figure 3). Only one station (~ ~~24 °N~~ 40 °W) had a negative CH_4 flux, which indicates a sink of CH_4. The overall average flux across the subtropical North Atlantic was~~is~~ 1.9 µmol m^{-2} d^{-1}. ~~Note, that~~However, ~~as a word of caution,~~it should be noted that the air-sea flux of CH_4 ~~depends~~ is dependant on the wind speed ~~, which~~and ~~means that values~~ can be locally different, varying~~change~~ depending on ~~location~~ specific weather conditions.

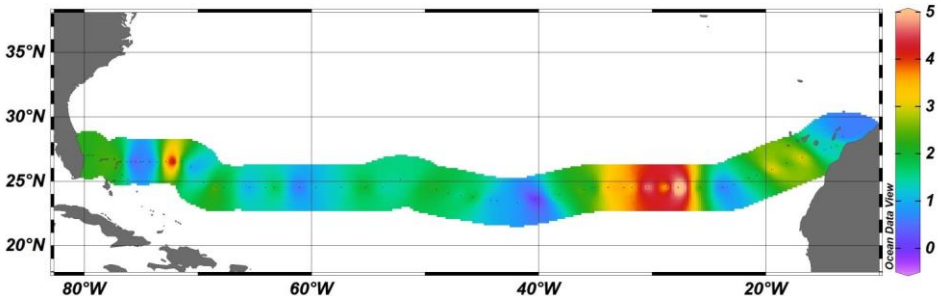

Figure 3. Sea-to-aAir CH_4 flux in , µmol m^{-2} d^{-1} along the cruise track of JC191. Dots indicate stations occupied by CTD casts.

Although sea-to-air flux of CH_4 presented here broadly agree with similar values of 1.6 µmol m^{-2} d^{-1} measured in the oligotrophic North Pacific, it can differ significantlysubstantially both temporarily and spatially. For instance, sea-to-air flux of CH_4 in the Sargasso Sea, also partly encompassed in the transect of JC191 is fluctuating between 1.6-4.4 µmol m^{-2} d^{-1}, depending on the season and weather conditions (Holmes et al., 2014). Furthermore, the base ecosystem at place substantiallycan -impact the s-sea-to-air flux of CH_4 if compared to other oceanic regions such as Belgic coastal zones with 1-160 µmol CH_4 m^{-2} d^{-1}(Borges et al., 2016) or Red Sea mangroves with 13.3 µmol CH_4 m^{-2} d^{-1} (Sea et al., 2018), or surveys in the east China Sea (6.5-7.4 4 µmol m^{-2} d^{-1}(Ye et al., 2015)) or the Golf of Mexico (0.38 µmol m^{-2} d^{-1} (Kelley and Jeffrey, 2002b)).Other studies report similar values for of 1.6 µmol m^{-2} d^{-1} sea-to-air CH_4 flux in the North Pacific. However this can differ significantly in other places, for example, sea-to-air CH_4 flux is 1.6-4.4 µmol m^{-2} d^{-1} in Sargasso Sea (Holmes et al., 2014); 1-160 µmol m^{-2} d^{-1} in Belgic coastal zones (Borges et al., 2016); 13.3 µmol m^{-2} d^{-1} in the Red Sea mangroves (Sea et al., 2018); 6.5-7.4 4 µmol m^{-2} d^{-1} in east China Sea (Ye et al., 2015); and 0.38 µmol m^{-2} d^{-1} in Golf of Mexico (Kelley and Jeffrey, 2002b).

4. Discussion

4.1 Methane distribution in surface waters of the subtropical North Atlantic Ocean

Our data across the subtropical North Atlantic Ocean unambiguously indicates an oversaturation in CH_4 of the surface layer (400 m) of 110 to 370%, which is in agreement with previous observations describing concentrations varying between 2-5 nmol/l with and maximum values of 10 nmol/l (Scranton and Brewer, 1977; Conrad and Seiler, 1988; Forster et al., 2009; de la Paz et al., 2015; Leonte et al. , 2020). This is also in line with previous observations that describinge the upper oceanic layer in subtropical areas of the global ocean as a source of CH_4 to the atmosphere (Reeburgh, 2007b; Dang and Li, 2018), in subtropical areas of the global ocean and also in some regions of the Arctic Ocean (Kitidis et al., 2010; Kudo et al., 2018). To

date, only the Southern Ocean is undersaturated in CH_4, although ~~this can be due to~~limited by the scarcity of data collected, highlighting ~~which~~the need of increased surveying~~s~~ to be complemented (Bui et al., 2018).

The distribution of dissolved CH_4 was variable across the subtropical North Atlantic with higher concentrations in the Eastern Basin (65-80 °W) and the Western Basin (15-30 °W) ~~contrasting with the~~and lowest concentrations measured in the central gyre system of the transect (30-65 °W) (Figure 2). The vertical distribution of CH_4 appears to be associated with fluorescence; highest concentrations of CH_4 were found at ~100 m depth, where fluorescence and dissolved oxygen are highest and nutrients levels lowest, which is in agreement with previous findings (Kudo et al., 2018).

~~We applied~~ PCA was applied to the datasets collected to identify which environmental parameters (nutrients, fluorescence, dissolved oxygen, temperature, salinity, depth, transmission) ~~could be~~are related to or influence the distribution of CH_4 along the transect. 54% of the variability could be explained by the first component ~~that~~ which is primarily controlled by depth (Figure 4). CH_4 is mainly associated with oxygenated surface waters, characterised by low concentrations of nutrients and a higher fluorescence. However, the weak contribution of CH_4 to the first two components may be due to the heterogeneity of its distribution. To fully understand the relationship between the different parameters controlling the distribution of CH_4, we therefore separated the transect into three main regions, i.e. i) the Western Basin, ii) the Central Gyre System and iii) the Eastern Basin. The PCA applied ~~on~~ to the regionalized dataset (Figure 5) revealed, that CH_4 is clearly associated to the abundance of primary producers in surface waters (<100m) in the western basin, while in the central gyre and eastern basin CH_4 concentrations were also influenced either by *in-situ* physical processes such as mixing or mesoscale eddies ~~at 400 m~~ (Kudo et al., 2018) or by external inputs ~~from the bottom~~ such as the Mauritanian upwelling that ~~brings~~ supplies CH_4-enriched waters to the upper layer (Conrad and Seiler, 1988).

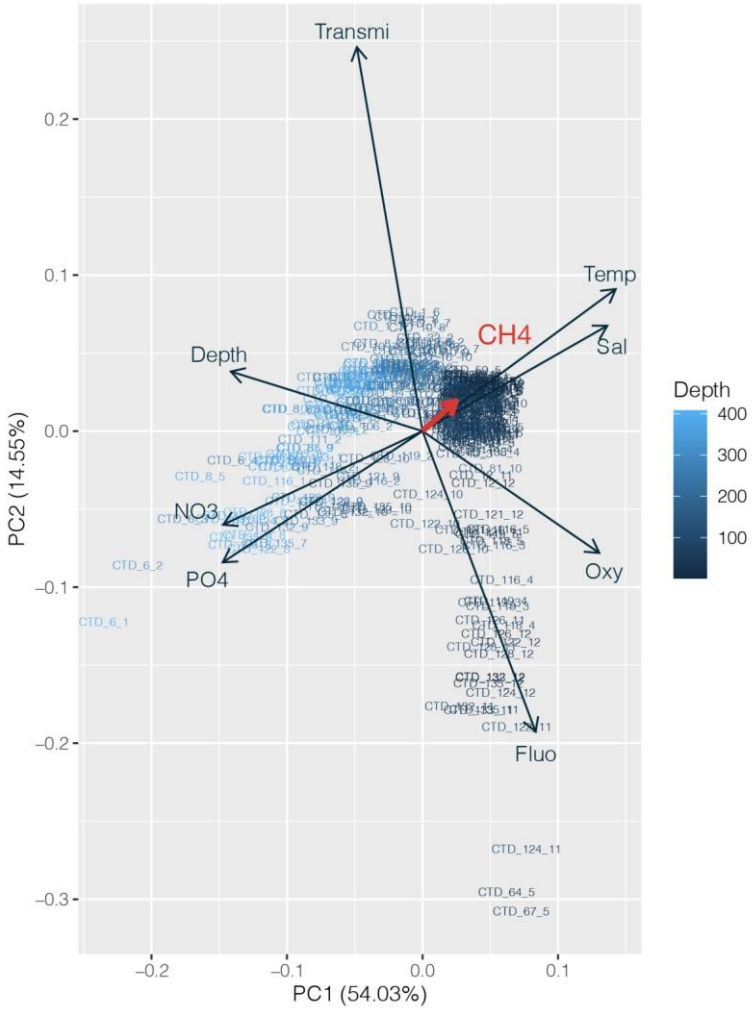

Figure 4: Principal Component Analysis (PCA) between dissolved CH_4 concentrations (in red) and other physico-chemical parameters (nutrients, depth, fluorescence, temperature, salinity and turbidity). Numbers on the x and y axes indicate the factor loadings of each variable of each principal component (PC). The percentages show the explained variability in the dataset by each PC.

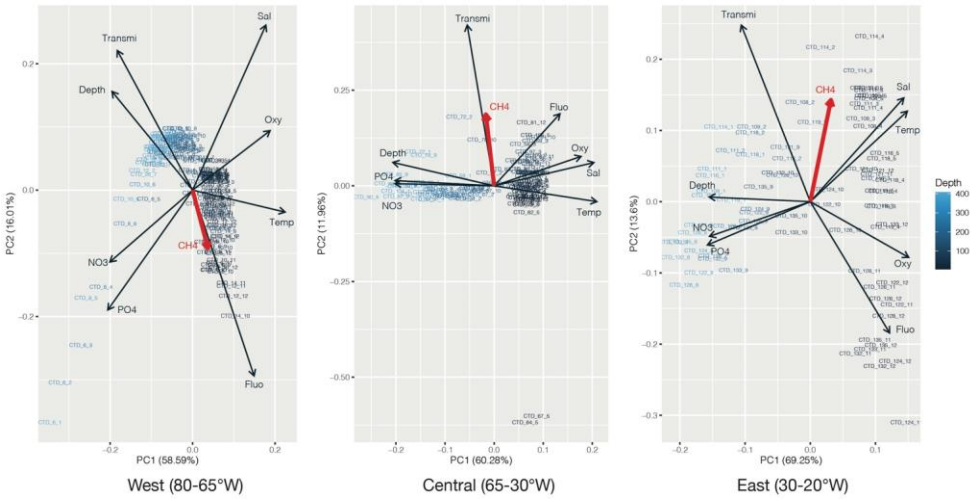

Figure 5: Principal Component Analysis on the regionalized dataset: west (80-65°W), central (65-30°W) and east (30-20°W). Numbers on the x and y axes indicate the factor loadings of each variable of each principal component (PC). The percentages show the explained variability in the dataset by each PC. CH_4 is highlighted in red.

Although CH_4 appeared to have a uniform vertical distribution (Figure 2), selected profiles from two areas of interest, CTD 50 (69,5 ºW, 24.9 ºN) and CTD 122 (20,8 ºW, 25,45 ºN) of CH_4, Chl *a*, phosphate and dissolved oxygen showed that the highest concentration of CH_4 in fact correspond to the maxima of Chl *a* and dissolved oxygen and the lowest concentrations of phosphate (Figure 6). The correlation between CH_4 and Chl *a* (Kendall rank correlation test, r2=, $p<0.05$) further suggests that the primary producers play a role in the production of CH_4.

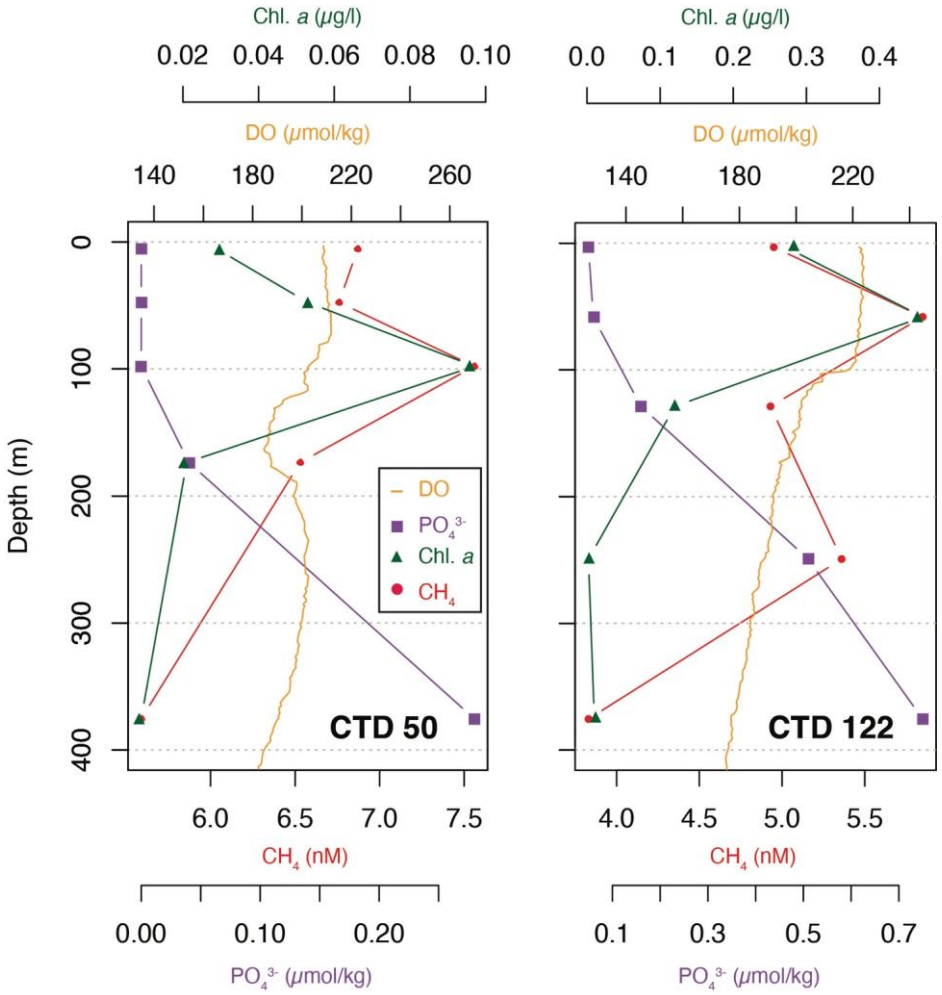

Figure 6. Selected data from CTD 50 (69.5 ºW, 24.9 ºN) and CTD 122 (20.8 ºW, 25.45 ºN) of CH_4 (red circles), Chl *a* (green triangles), phosphate (purple squares) and dissolved oxygen (orange).

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At station 50, the relationship between CH_4, Chl *a* and phosphate appears to be linear, e.g. CH_4 concentration decreasing as Chl *a* decreases and phosphate increases; while at station 122 CH_4 concentration showed a nonlinear pattern. It is not clear why CH_4 concentrations are variable but zooplankton grazing could potentially have a substantial impact (Simon et al., 2012). A possible influence of gas seeps on the CH_4 concentration is negligible as gas seeps only influence CH_4 concentrations in the immediate water column 100 to 150 m above the seeps (Leonte et al. 2020). Below 250 m water depth, CH_4 concentrations are decreasing, corresponding to an increase in phosphate and minimal Chl *a* concentrations, again suggesting the influence of primary producers (Brown et al., 2014).

4.2 Methane production linked to ~~a primary producers~~primary production

Autotrophic cyanobacteria *Prochlorococcus* and *Synechococcus* represent a major constituent of primary production in the subtropical North Atlantic, their distribution however differs greatly (Flombaum et al., 2013). Whereas *Synechococcus* solely occupies surface waters up to depths of ~ 100 m, *Prochlorococcus* occupies the whole water column, with deep-water maxima just above MLD, therefore responsible for fluorescence maxima at 100 to 130 m. The longitudinal distribution also differs between both taxa: The distribution of *Synechococcus* is limited to coastal, nutrient richer waters (Figure 7), whereas *Prochlorococcus* dominates the community throughout the transect (Figure 8).

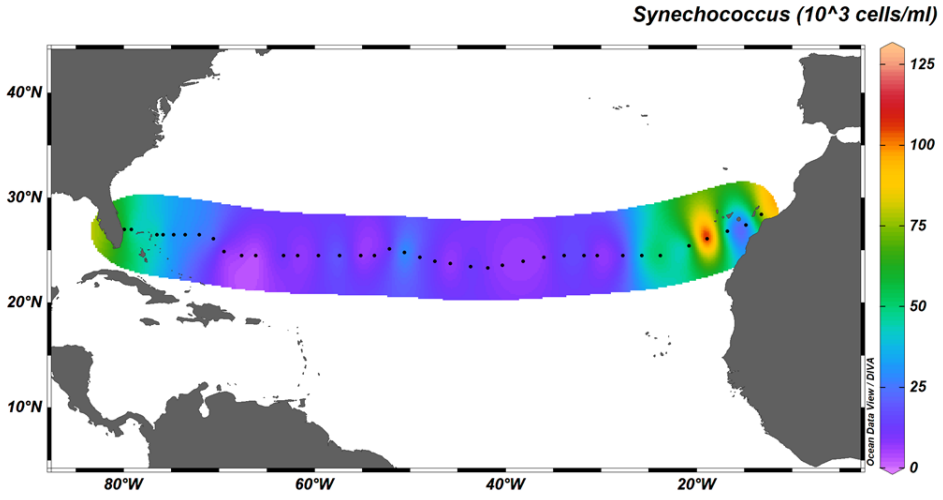

Figure 7. Depth-integrated abundance of *Synechococcus* (in 10^3 cells/ml) above MLD. Black dots represent the 38 out of the total 135 stations sampled for cyanobacterial abundance.

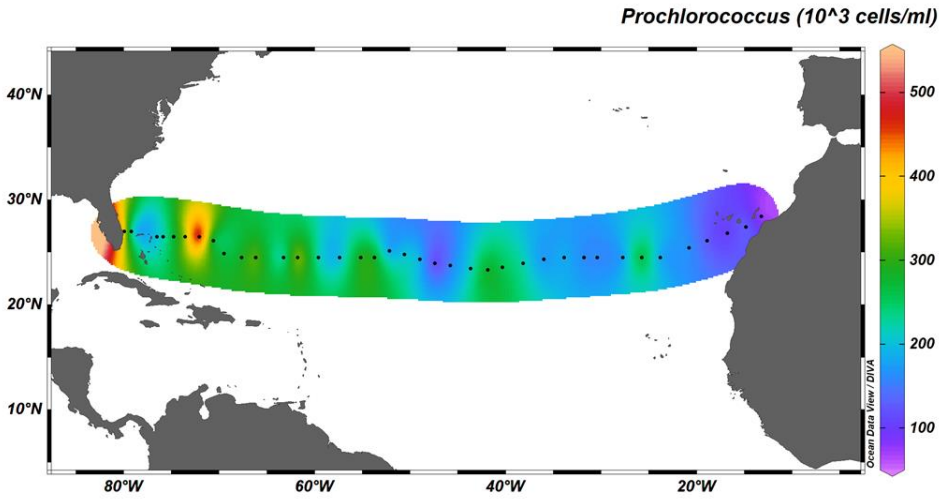

Figure 8. Depth-integrated abundance of *Prochlorococcus* (in 10^3 cells/ml) above MLD. Black dots represent the 38 out of the total 135 stations sampled for cyanobacterial abundance.

CH_4 distribution across the subtropical north Atlantic suggests the influence of the cyanobacterial community present; highest CH_4 concentrations were found 1) at DCM in the central gyre system, where *Prochlorococcus* is the predominant genus and 2) at the gyre boundaries, where higher abundances of both *Prochlorococcus* and *Synechococcus* were found. A PCA applied on the dataset including abundances of both cyanobacteria ~~(Figure 9) confirms this trend~~strengthens the conclusion that~~:~~ CH_4 production appears to be associated to primary production (Figure 9). ~~However, *in-situ* production of CH_4 is difficult to assess, due to the complexity of biogeochemical and physical processes involved in the marine CH_4 flux, mainly associated with *Synechococcus* and in a lesser extent with *Prochlorococcus*. Laboratory based studies with *Prochlorococcus* and *Synechococcus* confirmed a substantial production of CH_4 of up to 0.51 ± 0.26 µmol g^{-1} $hour^{-1}$ (Bižić et al., 2020).~~

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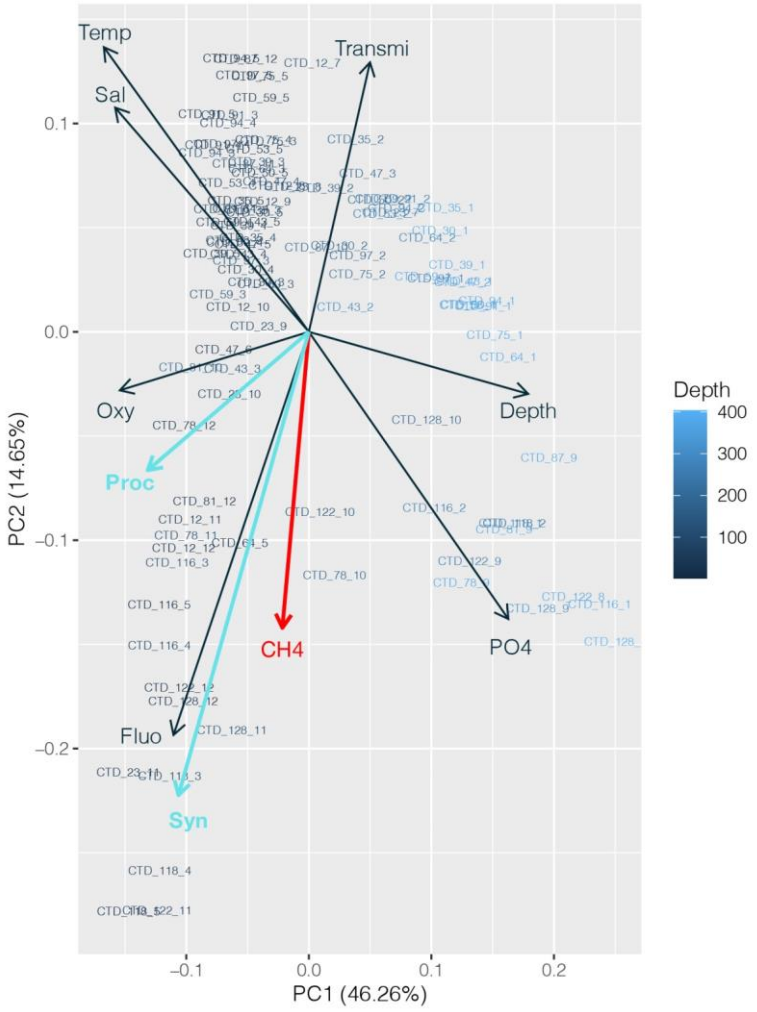

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Figure 9. Principal Component Analysis (PCA) between dissolved CH_4 concentrations (red), *Prochlorococcus* and *Synechococcus* abundances (light blue) and other physico-chemical parameters (nutrients, depth, fluorescence, temperature, salinity and turbidity). Numbers on the x and y axes indicate the factor loadings of each variable of each principal component (PC). The percentages show the explained variability in the dataset by each PC.

Not only do the bordering Gulf Stream to the West and the Canary Stream to the East provide a resupply of nutrients, and therefore support a greater abundance of cyanobacteria; the Canary Stream presents a pathway for the horizontal transfer of organic matter ~~-~~from the North African coast to the open ocean. Previous studies confirm high OM production in the eastern Subtropical North Atlantic as a result of the high rates of primary production fuelled by the Mauritanian upwelling (Reynolds et al., 2014). The transmission data (Figure 2h) suggests the export of organic matter throughout the eastern basin, which could contain MPn and thus a potential source of CH_4. Elevated CH_4 concentrations are mainly limited to the highly productive boundary systems, whilst the central gyre which lacks a sufficient resupply of bioavailable nutrients due to its downwelling nature, results in a decreased abundance of both *Prochlorococcus* and *Synechococcus* and henceforth decreased CH_4 concentrations (Figure 2a). In this especially P limited region, alternative nutrient sources such as the degradation of DOM to access organic phosphorus compounds become increasingly important in order for the cyanobacteria to meet their nutrient needs. The degradation of dissolved organic phosphorus via alkaline phosphatases (AP) such as *phoA* or *phoX* and the overexpression of the phosphate binding protein (pstS) have been believed to be the main adaptations to P-stress (Luo et al., 2009; Cox and Saito, 2013; Sebastian and Ammerman, 2009). Recently however, evidence was brought forth that some strains of *Prochlorococcus* can also oxidise MPn and other higher phosphonate compounds while releasing formate and potentially CH_4 as a by-product (Sosa et al., 2019a). Phosphonates are notably abundant and enriched in DOM (Sosa et al., 2019b) and their degradation releases considerable amounts of CH_4. *Prochlorococcus* and *Synechococcus* are the most abundant primary producers in the oligotrophic ocean, and as such produce considerable amounts of semi-labile DOM; both can synthesize phosphoenolpyruvate mutases (*pepM*) and therefore the DOM produced carries an enriched pool of MPn (Repeta et al., 2016; Sosa et al., 2019a). However, the metabolism of MPn is heavily regulated by bioavailable phosphate, thus the metabolic pathway of *pepM* might be heavily down regulated in the subtropical North Atlantic, whereas under replete conditions i.e. in the North Pacific *Prochlorococcus* can allocate up to 40 % of its internal P-quota towards phosphonate synthesis (Acker et al., 2022). Yet, the trait to produce phosphonates is located on genomic islands and is subject to horizontal gene transfer and can be frequently exchanged among marine microbial communities, hence also proteobacteria such ~~as the SAR11~~ *Pelagibacter spp.* in the SAR11 clade ~~clade~~ obtain *pepM* and are able to produce phosphonates (Acker et al., 2022). Similarly is the trait of phosphonate consumption subject to horizontal gene transfer and high-light strains of *Prochlorococcus* carry both production ~~Figu~~and consumption traits, therefore can also utilise MPn as alternative P source (Acker et al., 2022). The demethylation of MPn is mostly attributed to occur under P limiting conditions, such as in oligotrophic oceanic regions and further,~~Nonetheless,~~ most MPn oxidation and subsequent release of CH_4 is due to bacterial degradation of DOM and the breakdown of high energetic carbon-phosphorus bonds via C-P lyases, which are encoded by the *phn* operon, with transport systems including *phnC*, *phnD* and *phonE* and *phnJ* responsible for the cleavage of the C-P bond (Sosa et al., 2020). C-P lyases are abundant among *Pelagibacter spp*. and other alpha and ~~gammaproteobacteria~~gamma proteobacteria and can be found in ~ 50 % of organisms in the North Atlantic, where DOP concentrations are 4 fold lower in respect to the North Pacific (Sosa et al., 2020). Carini et al. (2014) estimated a potential production of 0.01-0.05 nM CH_4 per day by *Pelagibacterales* via C-P cleavage within

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the MPn pathway (Carini et al. 2014). However, due to complex biogeochemical and physical processes involved, *in-situ* production of CH_4 is difficult to assess and quantifying the individual contribution of primary producers towards CH_4 production was not the primary scope of the work presented. Here, the focus was to link the distribution of CH_4 in the subtropical North Atlantic to two vastly abundant cyanobacteria as exemplary primary producers, *Prochlorococcus* and *Synechococcus*, in order to draw conclusions which might explain the ocean methane paradox. Many mechanisms and precursors of oceanic *in-situ* production of CH_4 remain unknown and it is unclear, whether cyanobacteria such as *Prochlorococcus* or *Synechococcus* are ~~producing~~responsible for the release of CH_4 mainly via the degradation of MPn or indirectly by producing semi-labile DOM containing MPn cleaved by the bacterial community. Furthermore, recent laboratory-based studies also confirmed, that planktonic organisms produce CH_4 per se under high light intensities; *Prochlorococcus* showed a higher potential in CH_4 production than *Synechococcus*, with 0.8-110 pmol and 0.01-0.6 pmol CH_4 per 10^6 cells per hour respectively, larger cyanobacteria such as *Microcystis spp.* exceeded this by up to 0.51 ± 0.26 µmol/g per hour (Bižić et al., 2020).

Nonetheless, *Prochlorococcus* alone produces a gross ~22 nM CH_4 per day and therefore contributes substantially to the supersaturation of oligotrophic oceanic regions (typically between 7-25 nM) and to the over saturated state measured here (up to 10 nM) in the subtropical North Atlantic (Bižić et al., 2020). Cyanobacteria can greatly influence and potentially control CH_4 production in the marine environment, although other marine organisms such as different bacterial clades or coccolithophores are believed to also contribute to overall CH_4 production. N~~n~~itrogen fixing diazotrophs such as *Trichodesmium spp.* or *Rhodopseudomonas palustris* may contribute ~~to CH_4 production~~even to a higher degree (Bižić-Ionescu et al., 2018) and although spatially limited with *Trichodesmium spp.* dominating the western basin and *Hemilaulus* associated *Richelia* symbionts more so in the eastern basin (Luo et al., 2009), they are also abundant throughout the subtropical North Atlantic, ~~with *Trichodesmium spp.* dominating the western basin and *Hemilaulus* associated *Richelia* symbionts more so in the eastern basin (Luo et al., 2009)~~. *Trichodesmium* has higher nutrient requirements and can therefore outcompete cyanobacteria in uptake of inorganic nutrients and degradation of alternative sources; yet, energy intensive diazotrophic nitrogen fixation is controlled by micronutrients such as iron (Macovei et al., 2019) and is primarily occurring in the western basin, an area of high iron input by aeolian plumes originating from the Saharan desert (Ratten et al., 2015; Reynolds et al., 2014). Lastly, coccolithophores such as the ubiquitous abundant *Emiliania huxleyi* can also produce CH_4 (between 0.7-3.1 ± 0.4 CH_4 per gram POC per day (Lenhart et al., 2016b) (Klintzsch et al. 2019)) from ~~D~~DOM degradation ~~(Lenhart et al., 2016b)~~, and are believed to increase in abundance in the subtropical North Atlantic with increasing CO_2 concentrations at the air-sea interface due to further anthropogenic perturbation of the atmospheric CO_2 budget (Krumhardt et al., 2015).

Nonetheless, the data presented here suggest that the cyanobacterial community most likely plays a significant key role in the CH_4 flux in surface waters and the degradation of MPn from semi-labile DOM, ~~contributing~~helping to explain the methane paradox and henceforth the sea-air flux of CH_4 (Sosa et al., 2019a). Further investigation needs to focus on gathering *in-situ* data and should also include future scenarios, considering future climate and whole ecosystem community responses to consequences of altered climate conditions. The base ecosystem, specifically in P-limited regions is ever changing and highly

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adapted and horizontal transfer of genomic traits of P acquisition via various genomic pathways might become inherently important. Further work should also be considered in regards to mesocosm incubation studies with *in-situ* communities of natural composition to improve our understanding of the various processes and interactions involved in oceanic CH_4 production linked to primary producers to explain the ocean methane paradox.

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~~Although it remains broadly unclear whether cyanobacteria such as *Prochlorococcus* or *Synechococcus* are producing CH_4 mainly via the degradation of MPn or indirectly by producing semi-labile DOM containing MPn cleaved by the bacterial community, cyanobacteria can greatly influence CH_4 production in the marine environment. Furthermore, nitrogen-fixing diazotrophs may contribute to CH_4 production to a higher degree (Bižić-Ionescu et al., 2018) and are also abundant throughout the subtropical North Atlantic, with *Trichodesmium spp.* dominating the western basin and *Hemilaulus* associated *Richelia* symbionts more so in the eastern basin (Luo et al., 2009). *Trichodesmium* has higher nutrient requirements and can therefore outcompete cyanobacteria in uptake of inorganic nutrients and degradation of alternative sources; yet, energy intensive diazotrophic nitrogen fixation is controlled by micronutrients such as iron (Macovei et al., 2019) and is primarily occurring in the western basin, an area of high iron input by aeolian plumes originating from the Saharan desert (Ratten et al., 2015; Reynolds et al., 2014). Lastly, coccolithophores such as the ubiquitous abundant *Emiliania huxleyi* can also produce CH_4 from DOM degradation (Lenhart et al., 2016b), and are believed to increase in abundance in the subtropical North Atlantic with increasing CO_2 concentrations at the air-sea interface due to further anthropogenic perturbation of the atmospheric CO_2 budget (Krumhardt et al., 2015).~~

~~Nonetheless, the data presented here suggest that the cyanobacterial community could play a key role in the CH_4 flux in surface waters and the degradation of MPn from semi-labile DOM, contributing to explain the methane paradox and henceforth the sea-air flux of CH_4 (Sosa et al., 2019a). Further investigation needs to focus on gathering *in-situ* data and should also include future scenarios, considering future climate and whole ecosystem community responses to consequences of altered climate conditions. The base ecosystem, specifically in P-limited regions is ever changing and highly adapted and horizontal transfer of genomic traits of P acquisition via various genomic pathways might become inherently important.~~

5 Conclusions

Our study ~~shows~~ demostrates that the subtropical North Atlantic Ocean does indeed act as a source of CH_4 to the atmosphere, most likely controlled by cyanobacteria which are the dominant primary producers in ~~th~~the~~e~~ surface waters. Yet, anomalies found at depths below 200 m could also be attributed to the degradation of sinking organic material. The concentrations of dissolved CH_4 in this study were considerably higher near shelf regions and in the eastern boundary under the influence of the Mauritanian upwelling. The accumulation of organic matter and nutrients in these areas provide favourable conditions for both aerobic and anaerobic CH_4 production. It is expected that with increasing stratification and subsequent reduction in nutrient supply to the surface oligotrophic North Atlantic Ocean, the prevailing P-limitation will be further exacerbated, whereas coastal and shelf regions with increasing anthropogenic inputs of nutrients, could experience more frequent cyanobacterial blooms which, will in turn enhance CH_4 production (Dang and Li, 2018).

6. Author Contributions

Anna Kolomijeca – carried out dissolved gas sample~~s~~ collection, measurements and data analysis ~~of the dissolved gases included methane~~ and drafted the final manuscript

Lukas Marx – carried out phytoplanktonic sample collection, measurements and data analysis and drafted the final manuscript

Sarah Reynolds – helped in preparation of the cruise, measurements and data analysis, supervised biological part of the ~~experiments~~survey

Thierry Cariou - carried out nutrient ~~distribution study~~sample collection, measurements and data analysis

Edward Mawji - carried out nutrient ~~distribution study~~sample collection, measurements and data analysis

Cedric Boulart – helped to plan and prepare for the cruise, ~~helped with~~ result~~s~~ evaluation and provided overall project supervision

All authors contributed equally to the manuscript writing and had substantial input to the final version.~~.~~

7. Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

8. Funding

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A Kolomijeca's participation to the cruise ~~as well as~~and dissolved gas analyses were funded by the Region Bretagne SAD 470 'FULMAR' project, the ~~Fondation~~Foundation Air Liquide SMIS-4M project and the CNRS (LEFE Memestra).

L. Marx's and Sarah Reynolds' participation was funded by the University of Portsmouth PhD bursary scheme and a UK NERC National Capability programme CLASS (Climate Linked Atlantic ~~Sectore~~Sector Science) ECR fellowship.

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