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Biogeochemical Characteristics of Western Tropical Atlantic Ocean Water Masses

Características Biogeoquímicas das Massas de Água do Oceano Atlântico Tropical Oeste

Renan Evangelista Vieira[1,2], Leticia Cotrim da Cunha[1,2], Luana Keiroz Pinho[2], Alexandre Macedo Fernandes[1,3], Raquel Avelina[1,2], Ricardo de Almeida Keim[2], Carlos Musetti de Assis[1,2], Thiago Veloso Franklin[1,2], Jessica da Silva Nogueira[2]

[1] Universidade do Estado do Rio de Janeiro, Faculdade de Oceanografia, Programa de Pós-Graduação em Oceanografia, Rio de Janeiro, RJ, Brazil

[2] Universidade do Estado do Rio de Janeiro, Faculdade de Oceanografia, Laboratório de Oceanografia Química, Rio de Janeiro, RJ, Brazil

[3] Universidade do Estado do Rio de Janeiro, Faculdade de Oceanografia, Departamento de Oceanografia Física e Meteorologia, Rio de Janeiro, RJ, Brazil

Emails: vieira.renan_1@posgraduacao.uerj.br; lcotrim@uerj.br; luana.pinho@uerj.br; alexandre.fernandes@uerj.br; santos.raquel@posgraduacao.uerj.br; ricardo-keim@hotmail.com; assis.carlos@posgraduacao.uerj.br; franklin.thiago@posgraduacao.uerj.br; jessica.snogueira15@gmail.com

Corresponding author: Renan Evangelista Vieira; vieira.renan_1@posgraduacao.uerj.br

Abstract

Water masses are commonly identified according to their conservative parameters. However, there are also studies that use non-conservative parameters, together with the conservative ones, to refine the water masses identification. The aim of this study was to analyze the chemical properties of the water masses in the western tropical Atlantic Ocean (WTAO) according to their inorganic nutrient concentration: nitrate-NO_3^-, phosphate-PO_4^{3-}, and silicic acid-$Si(OH)_4$, to set a regional descriptive framework of the water column in view of future comparative studies. We collected full-depth water column samples from 18 oceanographic stations from a latitudinal transect along 38°W, from 02°S to 15°N during the PIRATA-BR XVII and XVIII campaigns, in November 2017 and 2018. We have also used the regional data available from GLODAPv.2 data product to improve the water masses characterization. Six water masses were identified in the region based on their values of potential temperature, salinity, potential density, and neutral density observed in the study area according to the CTD-O_2 data: Tropical Surface Water (TSW); South and North Atlantic Central Water (SACW and NACW, respectively); Antarctic Intermediate Water (AAIW); North Atlantic Deep Water (NADW); and Antarctic Bottom Water (AABW). Regarding the nutrient content within each water mass, our results showed that TSW corresponds to a surface oligotrophic water; NACW and SACW have intermediate nutrient concentration values between TSW and AAIW; AAIW showed the highest concentration of phosphate-PO_4^{3-} (~ 1.35 μmol kg^{-1}) and nitrate-NO_3^- (~ 30 μmol kg^{-1}); AABW, on the other hand, was the water mass with the highest silicic acid-$Si(OH)_4$ concentration (~ 80 μmol kg^{-1}), as well as high nitrate-NO_3^- (~ 25 μmol kg^{-1}) and phosphate-PO_4^{3-} (~ 1.80 μmol kg^{-1}) concentrations. Additionally, the water column between 300 and 650 m displays an increase in phosphate-PO_4^{3-} concentrations north of 5°N, associated to a low dissolved oxygen area coupled to the North Equatorial Under Current (NEUC). Long-term, sustained hydrographic and ocean biogeochemistry observations are key to understand how climate change is affecting the ocean, and this study is a contribution to that.

Keywords: Inorganic nutrients; Antarctic Intermediate Water (AAIW); Antarctic Bottom Water (AABW)

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Resumo

Massas de água são comumente identificadas de acordo com seus parâmetros conservativos. No entanto, também há estudos que usam parâmetros não-conservativos, junto aos conservativos, para refinar a identificação de massas de água. Neste estudo foram caracterizadas as propriedades químicas das massas de água no oceano Atlântico Tropical Oeste, de acordo com sua concentração de nutrientes inorgânicos dissolvidos: nitrato-NO_3^-, fosfato-PO_4^{3-} e ácido silícico-$Si(OH)_4$, a fim de estabelecer um quadro descritivo regional da coluna d'água tendo em vista futuros estudos comparativos. Foram coletadas amostras de água em um total de 18 estações oceanográficas ao longo do transecto 38°W, de 02°S a 15°N, durante as campanhas PIRATA-BR XVII e XVIII, em novembro de 2017 e 2018. Para auxiliar na caracterização das massas d'água, foram também analisados dados regionais disponíveis no produto de dados GLODAPv.2. Seis massas de água foram identificadas na região com base em seus valores de temperatura potencial, salinidade, densidade potencial e densidade neutra observadas na área de estudo de acordo com os dados do CTD-O_2: Água Tropical Superficial (AT); Águas Centrais do Atlântico Sul e do Atlântico Norte (ACAS e ACAN, respectivamente); Água Intermediária Antártica (AIA); Água Profunda do Atlântico Norte (APAN); e Água de Fundo Antártica (AFA). Em relação ao teor de nutrientes em cada massa d'água, nossos resultados mostraram que a AT corresponde a uma água oligotrófica superficial; as Águas Centrais ACAN e ACAS apresentam baixa concentração de nutrientes, mostrando concentrações intermediárias de nutrientes entre a AT e a AIA; a AIA apresentou a maior concentração de fosfato-PO_4^{3-} (~ 1,35 µmol/kg) e de nitrato-NO_3^- (~ 30 µmol/kg); a APAN não apresentou alta concentração de nutrientes; já a AFA foi a massa de água que apresentou a maior concentração de ácido silícico-$Si(OH)_4$ (~ 80 µmol/kg), bem como uma elevada concentração nitrato-NO_3^- (~ 25 µmol/kg) e fosfato-PO_4^{3-} (~ 1,80 µmol/kg). Além disso, a coluna de água entre 300 e 650 m apresenta um aumento nas concentrações de fosfato-PO43– ao norte de 5°N, associado a uma área de baixo oxigênio dissolvido acoplada à Subcorrente Norte Equatorial. Em longo prazo, observações hidrográficas e biogeoquímicas oceânicas são essenciais para entender como as mudanças climáticas estão afetando os oceanos, e este estudo é uma contribuição para isso.

Palavras-chave: Nutrientes inorgânicos; Água Intermediária Antártica (AIA); Água de Fundo Antártica (AFA)

1 Introduction

The western tropical Atlantic Ocean (WTAO) water column is composed by water masses from different sources and transport processes (Azar et al. 2021; Pickard & Emery 1990), each one having their own physical properties (Tomczak & Large 1989). Water masses are formed in certain regions in the ocean, where they acquire the physicochemical properties that characterize them (e.g., Azaneu et al. 2013; Emery, 2001; Ferreira & Kerr, 2017; Kerr et al. 2018; Santos et al. 2016; Souza, Kerr & Azevedo 2018; Tomczak 1999). In terms of characterization, water masses are commonly identified by their thermohaline characteristics, such as temperature, salinity and density values, since these are conservative parameters (Emery 2001; Herrford, Brandt & Zenk 2017; Pond & Pickard 2013; Schott et al. 2003, 2005; Silva et al. 2010; Stramma & England 1999; Talley et al. 2011).

In the WTAO, the main water masses found in the first 1500 m of the water column are the Tropical Surface Water (TSW), which is distributed in the first 100 meters of the water column. It is strongly influenced by the exchange processes with the atmosphere (e.g. energy, momentum, gases) that occur in the ocean surface, which can change its properties (Emery 2019). Below the TSW, both South and North Atlantic Central Waters (SACW and NACW, respectively) occupy the same density range (Stramma & Schott 1999) and are found in two different regions marked by the Cape Verde frontal zone along 12°N in the eastern Atlantic (Peña-Izquierdo et al. 2015), being NACW warmer and more saline (Stramma & Schott 1999). The Antarctic Intermediate Water (AAIW) is formed in the surface region of the Antarctic Circumpolar Current in in the Southern Ocean and show a maximum dissolved oxygen in the South Atlantic, and a minimum salinity in both South and Tropical Atlantic (Stramma & Schott 1999).

Since TSW, SACW, NACW and the upper portion of the AAIW are found in the upper part (1500 m) of the water column in the WTAO, they are transported by the regional surface and subsurface current system. Among these currents are included the North Equatorial Current (NEC); the North Equatorial Undercurrent (NEUC); the North Equatorial Countercurrent (NECC), which is the result of the retroflexion of the North Brazil Current (NBC); and the South Equatorial Current (SEC) (Lumpkin & Garzoli 2005; Stramma et al. 2003; Stramma & England 1999).

In the deeper portion of the WTAO, below 1500 m, the main water masses found are the North Atlantic Deep Water (NADW), which presents high values of salinity and oxygen, and lower temperature, occupying a layer of approximately 2500 m in the deep ocean (Stramma & Schott 1999). The Antarctic Bottom Water (AABW), which is found south of the Mid-Atlantic Ridge in depths below 4000 m, is the densest and the coldest among the WTAO water masses (Herrford, Brandt & Zenk 2017; Silva et al. 2010). These deeper water masses are transported in the ocean according to the difference in their density values (Emery 2019; Herrford, Brandt & Zenk 2017; Silva et al. 2010).

Besides the thermohaline characteristics, non-conservative parameters can also be used to identify water masses, as they are almost conservative below the euphotic zone (Kress & Herut 2001). These parameters can be used as complementary tracers to refine the water masses identification, as well as elucidating what processes are occurring in the water mass. (Braga & Niencheski 2006; Kress & Herut 2001; Oudot et al. 1999; Sardessai et al. 2010). The most common biogeochemical parameter applied to characterize water masses is the dissolved oxygen concentration (Silva et al. 2010), but dissolved inorganic nutrients may also be used (Azar et al. 2021; Pérez et al. 1998; Souza, Kerr & Azevedo 2018).

Pérez et al. (1998) analyzed dissolved inorganic nutrients, along with dissolved oxygen and inorganic carbon in the upper and middle portions of the northeast subtropical Atlantic east of the Azores. High concentrations of nutrients in the AAIW were observed, indicating a strong remineralization. At the Equatorial Indian Ocean, Sardessai et al. (2010), identified four water masses according to nutrient concentrations together with physical parameters. The surface waters were characterized by having a high concentration of silicic acid-$Si(OH)_4$, while the Indian Central Water presented high concentrations of nutrients in its shallower depths.

More recently, Azar et al. (2021) studied the source waters contribution to the Tropical Atlantic's central layer, using nitrate-NO_3^- and phosphate-PO_4^{3-} concentration together with physical parameters. The study found that locally, the mixed fractions of SACW are mainly influenced by the mixing of the mode waters $STMW_{18}$ and $STMW_{12}$ displaced by the SEC, and only partially influenced by the Indian Ocean mode waters (STIMW) in the area close to the North Brazil Current. STIMW is likely isopicnally mixed with $STMW_{12}$ and enter the Atlantic Ocean through mesoscale eddies (Azar et al. 2021; Souza, Kerr & Azevedo 2018). Besides that, Azar et al. (2021) conclude that the North Atlantic subtropical mode water, Eighteen Degree Water (EDW), contributes to NACW upper portions, while the Madeira Modal Water (MMW) contributes to its lower portions.

It is noteworthy that there are not many recent studies aimed at the biogeochemical characterization of the water masses present in the Western Tropical Atlantic. Besides that, it is virtually certain that anthropogenic climate change has already warmed the upper ocean and decreased surface seawater pH, and there is high confidence that the ocean has lost part of its dissolved oxygen content since the last century (IPCC 2021). Other changes are expected such as increased stratification and reduction in water masses ventilation, which in turn enhances deoxygenation and affects nutrients availability in the photic zone, with consequences to the marine trophic web (Shepherd et al. 2017). In this context, this study presents a full-depth, western tropical Atlantic Ocean distributions of inorganic nutrients (nitrate-NO_3^-, phosphate-PO_4^{3-}, silicic acid-$Si(OH)_4$), dissolved oxygen, and physical properties (potential temperature, salinity, neutral density) along 38°W in a latitudinal section in 2017 and 2018. The goal of this work is to set a general oceanographic and biogeochemical framework for future regional water mass studies within PIRATA and other science programs aiming at understanding climate change effects such as ocean acidification and deoxygenation. Additionally, this study investigates how the use of inorganic nutrient concentrations could further help to identify and characterize the WTAO water masses.

These campaigns were part of the Prediction and Research Moored Array in the Tropical Atlantic project (PIRATA; Bourlès et al. 2019), coordinated by the National Institute for Space Research (INPE) in Brazil, with the support of the Brazilian Navy and the Ministry of Science, Technology and Innovation, and the participation of scientific teams from seven Brazilian public universities (UFPE, UERJ, UFF, UFBA, USP, FURG and UFC).

2 Materials and Methods

2.1 Data Acquisition

This study used data collected during the PIRATA-BR XVII and PIRATA-BR XVIII campaigns in November 2017 and November 2018, respectively, in a transect carried out aboard the Brazilian Navy RV *Vital de Oliveira* along the longitude 38°W, between latitudes 02°S and 15°N, with a latitudinal interval of 1° at each sampling station. In 2018, the stations located at 02°S and 05°N were not sampled due to bad oceanographic conditions to operate the rosette (Figure 1).

A Sea Bird Electronics® Inc. (SBE) CTD-Rosette set model SBE 911plus CTD-O_2 system was used to measure hydrographic parameters in the water column, such as temperature, salinity, dissolved oxygen, and fluorescence. Seawater for biogeochemical analyses was sampled with the aid of 22 twelve-liter Niskin bottles. Discrete water samples were collected from the Niskin bottles mounted in the rosette to determine nitrate-NO_3^-, phosphate-PO_4^{3-}, and silicic acid-$Si(OH)_4$ concentrations, and stored frozen in 100 mL polyethylene flasks until laboratory analyses. At each station, between 9 and 11 discrete samples at different depths were established for biogeochemistry analyses, according to the data from the CTD-O_2 profiles of salinity, temperature and dissolved oxygen.

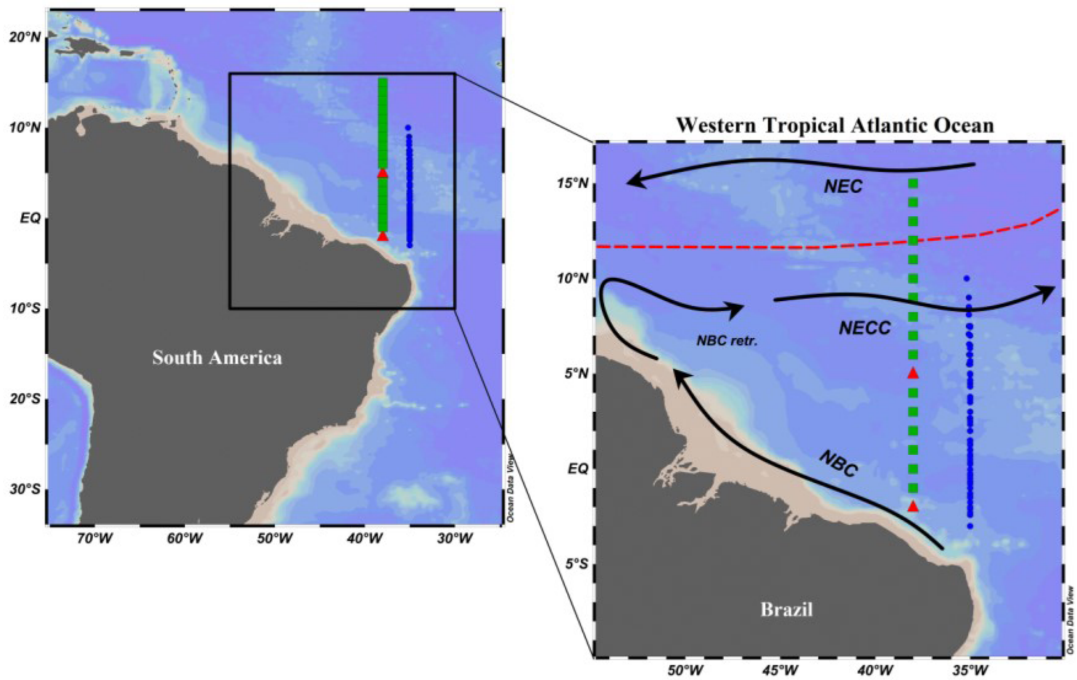

Figure 1 Map of the study area and sampling stations along the 38°W for PIRATA and 35°W for GLODAPv.2. The green squares and the red triangles correspond to the PIRATA stations, being in green the stations where we collected in 2017 and 2018; and in red the stations where samples were collected only in 2017. The blue dots correspond to the GLODAPv.2 data product stations. The red dashed line corresponds to the northern limit of the Intertropical Convergence Zone (ITCZ) during the austral winter period. The black arrows correspond to the main surface currents present in the WTAO region. The acronyms correspond to North Equatorial Current (NEC); North Equatorial Counter Current (NECC); North Brazil Current (NBC).

The data collected during the PIRATA campaigns were also compared with data available in the data product of the Global Ocean Data Analysis Project (GLODAPv.2) data product (Olsen et al. 2020). The GLODAPv.2 data used in this study are comprised in a transect along the longitude 35°W, monitored since the 1990s as part of the World Ocean Circulation Experiment (WOCE), between the latitudes 03°S and 10°N, which correspond to the vertical transect that has the largest database in the region (Chapman 1998). This section was chosen to be compared with the PIRATA dataset because it is the closest to the 38°W section with enough spatial and temporal coverage of sampling stations (from 1990 to 2010).

2.2 Laboratory Analysis

Nitrate-NO_3^-, phosphate-PO_4^{3-} and silicic acid-$Si(OH)_4$ concentrations for PIRATA-BR XVII campaign (2017) were determined in the laboratory of the Multi-User Environmental Analysis Unit at Federal University of Rio de Janeiro (UFRJ) using the spectrophotometric method described in Hansen & Koroleff (1999) in the FOSS automatic analyzer model FiaStar 5000 through flow injection analysis (FIA). The same spectrophotometric method was applied for PIRATA-BR XVIII samples, analyzed in the Chemical Oceanography Laboratory at Rio de Janeiro State University (UERJ).

Absorbance readings were performed using 880 and 810 and 540 nm as wavelength for phosphate-PO_4^{3-}, silicic acid-$Si(OH)_4$ and nitrite, respectively. The method accuracy is 0.01 µM for phosphate-PO_4^{3-}, 0.1 µM for silicate, and 0.02 µM for nitrite. The determination of nitrate-NO_3^- was performed by reducing it to nitrite using a copperized cadmium column. The total nitrite value in the sample (nitrite + reduced nitrate-NO_3^-) minus the nitrite value gives the concentration of nitrate-NO_3^- present in the sample.

2.3 Water Masses Identification

The initial identification of the water masses present in the region was carried out according to the thermohaline limits and values of potential temperature, salinity, potential density, and neutral density observed in the study area according to the CTD-O_2 data (Table 1).

The water masses were firstly identified by a T-S diagram, together with potential density isolines. Vertical section graphs with the neutral density variable isolines were created using Ocean Data View software (Schlitzer 2017), using the interpolation DIVA (Data-Interpolating Variational Analysis; Troupin et al. 2012), in order to observe the vertical distribution of the water masses along the PIRATA section (38°W) and the GLODAPv.2 data product along 35°W, as proposed by Herrford, Brandt & Zenk 2017.

Table 1 Characterization of water masses from their potential temperature (°C), salinity, potential density (σθ, kg m-3) and neutral density (γn, kg m-3) data. Water mass acronyms: TSW – Tropical Surface Water; SACW – South Atlantic Central Water; NACW – North Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water; AABW – Antarctic Bottom Water.

Parameter	TSW	SACW	NACW	AAIW	NADW	AABW	Reference
Potencial Temperature (°C)	---	6.55 – 16.27	6.99 – 13.90	---	2.10 – 4.30	0.50 – 1.80	Poole & Tomczak (1999)
Salinity	---	34.40 – 35.69	34.94 – 35.89	---	---	---	Poole & Tomczak (1999)
Potencial Density σ_θ (kg m^{-3})	< 24.50	26.00 – 27.00	---	26.95 – 27.50	27.72 – 27.88	> 27.88	Herrford, Brandt & Zenk (2017)
Neutral Density γ^n (kg m^{-3})	< 24.45	24.45 – 26.82	---	26.82 – 27.72	27.73 – 28.14	> 28.14	Liu & Tanhua (2019a)

2.4 Statistical Analysis

Different types of statistical analyzes were used in the Paleontological Statistics - PAST program (Hammer et al. 2001), version 3.25 of 2019. First, through the Shapiro-Wilk statistical test, the normality of the different biogeochemical parameters for the two datasets (PIRATA-BR XVII, XVIII) was tested in order to verify their distributions (Shapiro & Wilk 1965). Shapiro-Wilk test is, apparently, the best test of adherence to normality with a confidence level of 95% (Hammer et al. 2001). Through the p-values obtained for each of them, it was possible to observe that all parameters have a non-normal distribution ($p < 0.05$), mainly in the GLODAPv.2 data product, leading to the adoption of non-parametric comparison statistics (USA) (Supplementary Table S1).

The Kruskal-Wallis test, also available in the Past software, was applied to the three datasets to compare the nutrient distributions. This statistical test assesses if there is at least one among three or more groups of quantitative data that differ significantly from the others when the p-value is lower than 0.05 (Kruskal & Wallis 1952). To verify these values pairwise, water masses were also analyzed according to Dunn test (Sherman 1965), that determines that two groups differ significantly when the p-value of the comparative analysis is also less than 0.05 (Supplementary Table S2).

When the water masses did not show enough data points among PIRATA and GLODAP sections, the Wilcoxon-Mann-Whitney test was applied to compare only two data groups. The p-values <0.05 in this test also indicates samples from different groups (Fay & Proschan 2010) (Supplementary Table S2).

3 Results

3.1 Water Masses Identification

During both years of the PIRATA campaigns, according to the potential temperature, salinity and dissolved oxygen data measured by the CTD-O_2 system (Figs. 2A and 2B), it was possible to observe that the vertical structure of the water column in the region is represented by the following water masses: Tropical Surface Water (TSW); South Atlantic Central Water (SACW); North Atlantic Central Water (NACW); Antarctic Intermediate Water (AAIW); North Atlantic Deep Water (NADW); and Antarctic Bottom Water (AABW). The GLODAP oceanographic stations along 35°W, in turn, presented all water masses except NACW (Figure 2C).

Since both central water masses, SACW and NACW, share a very similar density range (Stramma & Schott 1999), the T-S diagrams were made with the Z axis established by the dissolved oxygen concentrations (Figures 2A and 2B), as SACW has a lower oxygen concentration compared to NACW (Stramma & Schott 1999). The horizontal boundary between these two water masses was limited according to the Cape Verde frontal zone, around 12°N (Peña-Izquierdo et al. 2015). While SACW presence is observed along 02°S to 10°N, NACW is found only north of 10°N in the study area. This was already expected because of the upper

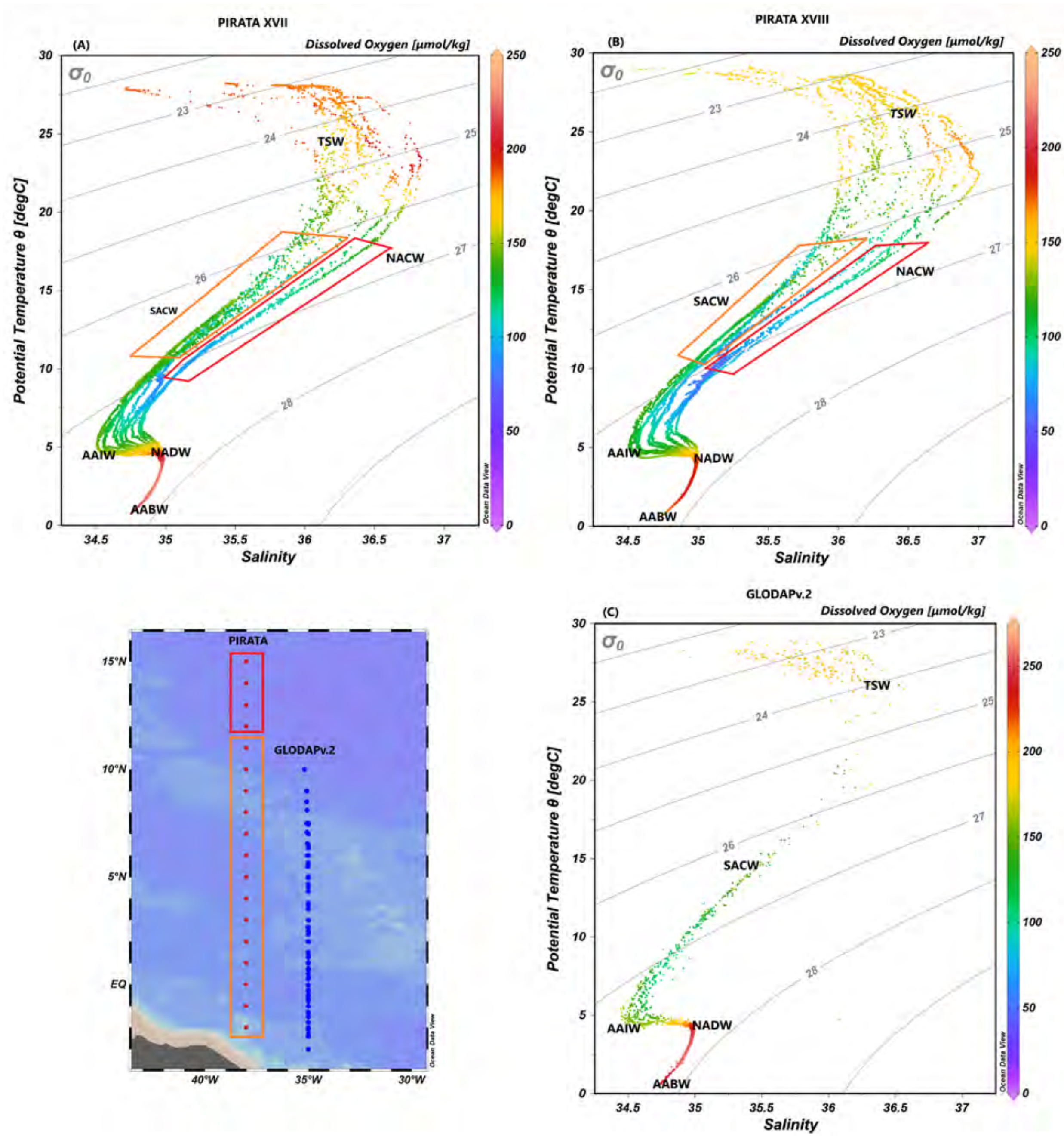

Figure 2 Potential temperature-salinity scatter (T-S) diagrams for PIRATA section 38°W campaigns in A. 2017; B. 2018; C. for GLODAPv.2 section 35°W dataset, collected between 1990 and 2010. Gray lines correspond to potential density anomaly (σ0). The acronyms correspond to Surface Tropical Water (TSW); South Atlantic Central Water (SACW); North Atlantic Central Water (NACW); Antarctic Intermediate Water (AAIW); North Atlantic Bottom Water (NADW); Antarctic Bottom Water (AABW). The colored bars correspond to dissolved oxygen concentration, in µmol kg–1.

complex circulation regime in area (Schott et al. 2005), and the presence of the eastern Atlantic Ocean the Cape Verde frontal zone, found around 12°N (Peña-Izquierdo et al. 2015), between approximately 100- and 200-meters depth. Thus, NACW was not observed in the GLODAPv.2 data product as these dataset does not extend beyond 10°N. As NACW was identified only in the two PIRATA campaigns, the Wilcoxon-Mann-Whitney test was applied to compare the nutrients concentrations between the two campaigns (2017 and 2018).

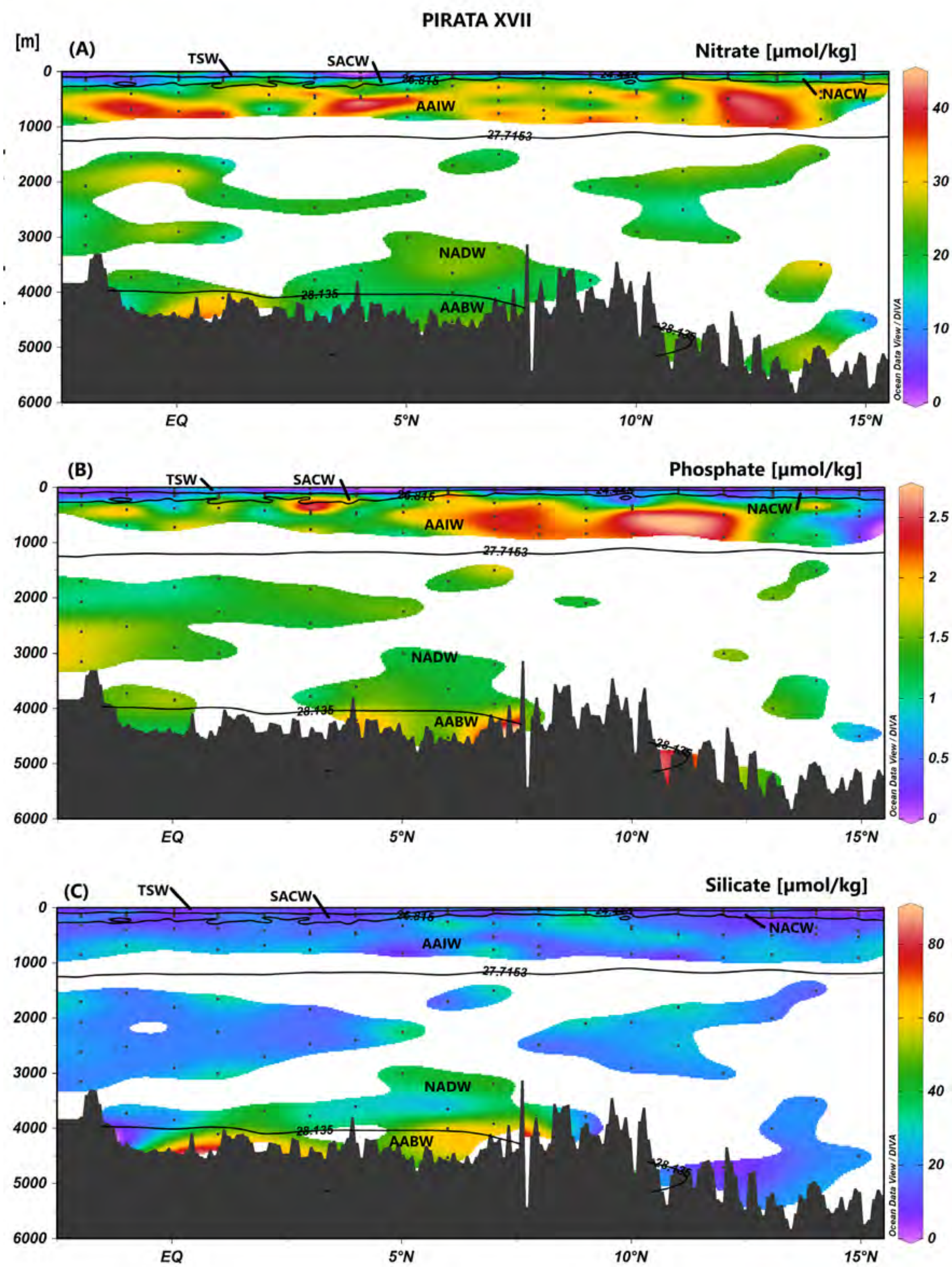

Figure 3 Vertical profiles for: A. nitrate-NO3– (µmol kg–1); B. phosphate-PO43– (µmol kg–1); C. silicic acid-Si(OH)4 (µmol kg–1) for PIRATA-BR XVII (2017), along the 38°W transect between 02°S and 15°N. The gray dots represent the sampling depths. The acronyms correspond to: TSW –Tropical Surface Water; SACW – South Atlantic Central Water; NACW – North Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water; AABW – Antarctic Bottom Water.

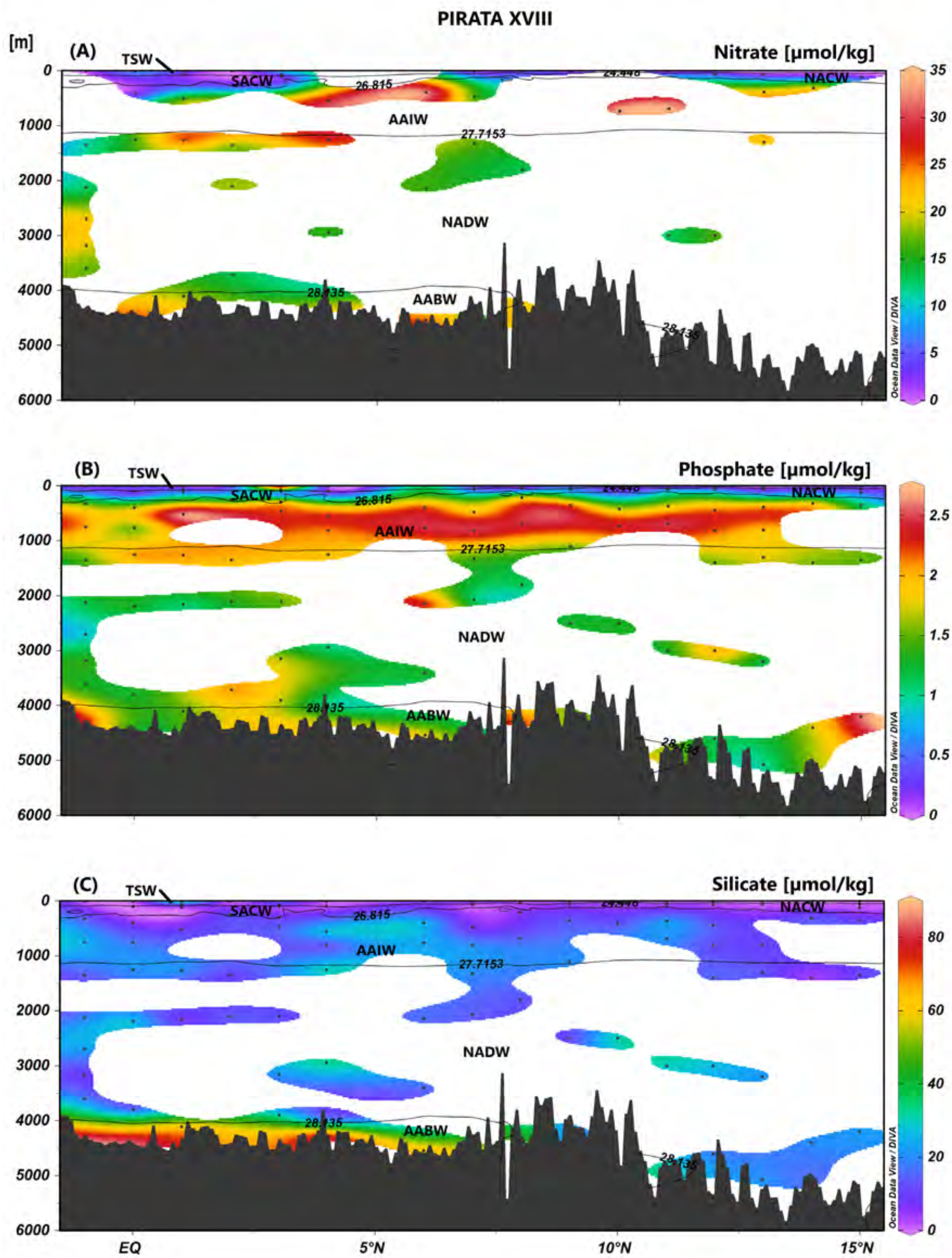

Figure 4 Vertical profiles for: A. nitrate-NO3– (µmol kg–1): B. phosphate-PO43– (µmol kg–1); C. silicic acid-Si(OH)4 (µmol kg–1) for PIRATA-BR XVIII (2018), along the 38°W transect between 2°S and 15°N. The gray dots represent the sampling depths. The acronyms correspond to: TSW –Tropical Surface Water; SACW – South Atlantic Central Water; NACW – North Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water; AABW – Antarctic Bottom Water.

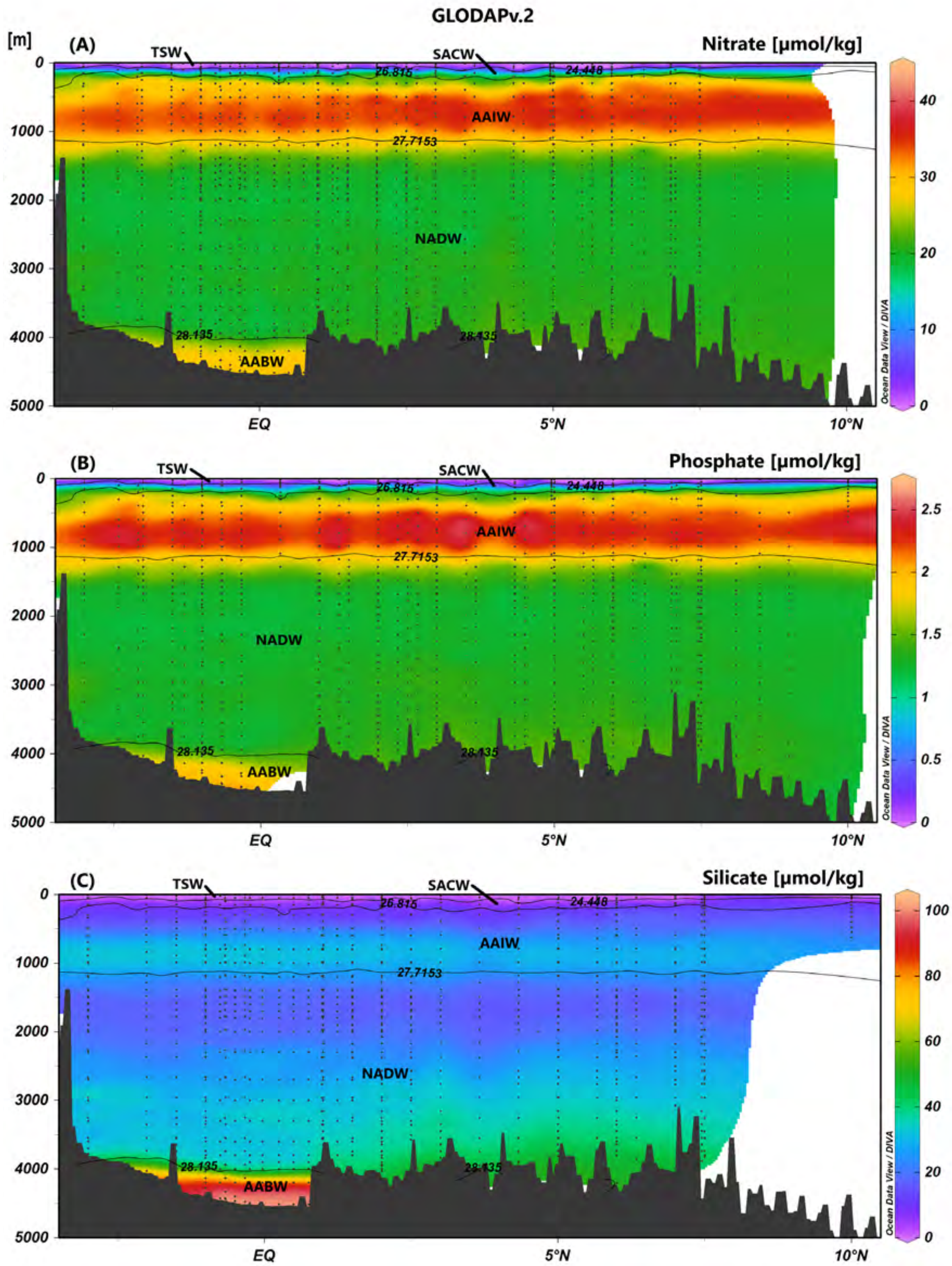

Figure 5 Vertical profiles of: A. nitrate-NO3– (μmol kg–1); B. phosphate-PO43– (μmol kg–1); C. silicic acid-Si(OH)4 (μmol kg–1), along the 35°W transect for GLODAPv.2, (1990 – 2010) between 3°S and 11°N. The gray dots represent the sampling depths. The acronyms correspond to: TSW – Tropical Surface Water; SACW – South Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water; AABW – Antarctic Bottom Water.

3.2 Dissolved Inorganic Nutrients Vertical Distribution

Dissolved inorganic nutrient concentration data for PIRATA-BR XVII and XVIII campaigns (Supplementary Table S3) were represented in vertical profiles using the Ocean Data View software (Schlitzer 2017), associated with the corresponding water masses present in the region (Figures 3, 4 and 5).

Nitrate-NO_3^- presented distinct concentrations along the water column with the lowest concentrations in TSW, being almost depleted. SACW and NACW showed small concentrations. AAIW is the water mass with the highest concentration of nitrate-NO_3^-. NADW showed just intermediate concentration values in comparison to other water masses. The AABW nitrate-NO_3^- concentration values are also high, although not as higher as the AAIW ones (Figures 3A, 4A and 5A; Supplementary Table S3).

Phosphate-PO_4^{3-} concentration showed a similar pattern compared to the nitrate-NO_3^- one. The TSW layer had the lowest concentrations, being also almost depleted nutrients. SACW and NACW central waters showed low phosphate-PO_4^{3-} concentrations while AAIW presented the highest phosphate-PO43– concentrations. NADW concentrations were intermediate in terms of phosphate-PO_4^{3-} while AABW phosphate-PO_4^{3-} concentrations were also high (Figures 3B, 4B and 5B; Supplementary Table S3).

The comparison among the water masses in WTAO in terms of silicic acid-$Si(OH)_4$ showed lower concentrations in the TSW, SACW and NACW; intermediate values in AAIW and NADW; and the highest concentrations in AABW (Figures 3C, 4C and 5C; Supplementary Table S3), being the most uniform nutrient distribution in the study area.

4 Discussion

Through the results obtained in this study, the water masses biogeochemical characteristics were evaluated to establish whether these features can be used as additional parameters to assist in their identification and application in future studies dedicated to understanding the source water masses variability in face of ocean warming, acidification and deoxygenation.

4.1 Tropical Surface Water

According to the results, in both PIRATA campaigns and in the GLODAPv.2 data product, TSW is observed in the surface of the ocean, approximately in the first 100 m, that corresponds to the oligotrophic zone, and is the water mass with the lowest average concentration of nitrate-NO_3^-, phosphate-PO_4^{3-} and silicic acid-$Si(OH)_4$, when compared to other water masses observed in the study region (Figures 3 and 4; Supplementary Table S3).

The oligotrophic western tropical Atlantic TSW receives high insolation and overlies a lower oxygen layer (Figure 2). In this region, photosynthetic organisms are nutrient-limited, although primary production can be occasionally fueled in the surface by atmospheric iron deposition and phosphate-PO_4^{3-} inputs from upwelling, triggering diazotroph blooms (Bristow et al. 2017). Aerobic nitrifier microorganisms are also limited by the low inorganic nitrogen and phosphate concentrations in this oligotrophic ocean region (Bristow et al. 2017; Zakem et al. 2018).

This result reinforces the findings that analyses of non-conservative parameters, as complementary water mass tracers are not suitable for application to water masses in the euphotic zone (Kress & Herut 2001).

4.2 South and North Atlantic Central Waters

While SACW presence is observed along 02°S to 10°N, NACW is found only north of 10°N in the study area. This was already expected because of the upper complex circulation regime in area (Schott et al. 2005), and the presence of the eastern Atlantic Ocean the Cape Verde frontal zone, found around 12°N (Peña-Izquierdo et al. 2015), between approximately 100 and 200 meters depth. Because of these two factors, NACW was not observed in the GLODAPv.2 data product as these dataset does not extend beyond 10°N, thus limiting the NACW biogeochemistry analysis to only PIRATA campaigns.

Compared to the intermediate and deeper water masses, the SACW has low nutrient concentration. Silicic acid-$Si(OH)_4$ does not vary when compared to TSW (above) and NACW (to the north). This lower variation of silicic acid-$Si(OH)_4$ concentrations along these three water masses challenges the identification and characterization through this parameter between them. However, compared to AAIW, it is possible to note that SACW has an average silicic acid-$Si(OH)_4$ concentration about 10 times lower (Supplementary Table S3), which may help to differentiate these two water masses. Nitrate-NO_3^- and phosphate-PO_4^{3-} concentrations are also good markers to separate SACW from underlying and overlying waters, since TSW is almost depleted in terms of nutrients, while AAIW shows the highest concentration for these nutrients.

Overall, NACW presented nitrate-NO_3^- concentrations slightly lower when compared to SACW. Some other differences can also be seen between the eastern portion of the Tropical Atlantic and the Western one in terms of all analyzed nutrients. According to Stramma & Schmidtko (2020) results, nitrate-NO_3^-, phosphate-PO_4^{3-} and silicic acid-$Si(OH)_4$ concentration means in two different areas in the Eastern Tropical Atlantic that corresponds to SACW (17.754, 7.523 and 1.148 µmol kg^{-1}, respectively) and NACW (22.518, 9.718 and 1.414 µmol kg^{-1}, respectively), between 50 and 300 m, verified that NACW region shows higher concentration.

These differences in the concentrations between the western and the eastern portion of the Tropical Atlantic were expected since it was verified by Levitus et al. (1993) that nutrient concentration decreases westwards in this region. This pattern could be a response to the oxygen minimum zone (OMZ) located off the African coast in the eastern tropical Atlantic, since this is a region where the dominant process is the upwelling and consequent remineralization of the organic matter produced in the surface, leading to an inverse behavior of nutrients and dissolve oxygen concentration (Whitney, Bograd & Ono 2013).

Through the North Equatorial Current (NEC), the western Tropical Atlantic receives the influence of the OMZ (Peña-Izquierdo et al. 2015). Since this current flows westward in the NACW region, from the surface and to the 400 m, and between 10 and 15°N (Lumpkin & Garzoli 2005; Stramma et al. 2003), it is also expected that the influence of the OMZ in the north would be higher, what could explain the higher nitrate-NO_3^- concentration found in NACW compared to the SACW.

4.3 Antarctic Intermediate Water

The AAIW in our study section was observed approximately between 200 and 1300 m, and it was the water mass that showed the highest concentrations of phosphate-PO_4^{3-} and nitrate-NO_3^-, and this can be seen in the PIRATA sections in both years and in GLODAPv.2 (Figures 3A, 3B, 4A, 4B, 5A and 5B; Supplementary Table S3), making both the best markers to separate AAIW from underlying and overlying waters.

In PIRATA XVII, nitrate-NO_3^- concentrations were higher, ranging from 20 to 40 µmol/kg (Figure 3A). In PIRATA XVIII, it is possible to observe in the section the presence of values distributed around 30 µmol kg^{-1} (Figure 4A). The GLODAPv.2 section, on the other hand, has a continuous distribution, with a large portion at the center of the water mass with concentrations of approximately 40 µmol kg^{-1} (Figure. 4A).

Phosphate-PO_4^{3-} had a very similar distribution to nitrate-NO_3^- in AAIW. The GLODAPv.2 and PIRATA XVIII data showed a very similar distribution (Supplementary Table S2), with the water mass concentration varying between 1.5 and 2.5 µmol kg^{-1} (Figures 4B and 5B). The AAIW core has the highest concentrations of phosphate-PO_4^{3-} (Figure 4B). During PIRATA XVII, it is possible to notice just one region of higher concentration (~ 2.3 µmol/kg) between latitudes 06 and 13°N, while the rest of the southern portion has values of approximately 1.5 µmol kg^{-1} (Figure 3B).

The distribution pattern for the phosphate-PO_4^{3-} observed in PIRATA XVII could also be associated to the dissolved oxygen distribution pattern in the western and central tropical Atlantic, which shows an extensive low concentration portion ($O_2 < 150$ µmol kg^{-1}) north of the 05°N. This dissolved oxygen pattern can be observed in the GLODAPv.2 data product (Figure 6), as well as in the study conducted by (Liu & Tanhua 2019b) in a transect from 60°S to 60°N in the Atlantic Ocean, matching the inverse relationship between nutrients and oxygen concentrations, and also suggesting the remineralization of the organic matter occurring in the region (Whitney, Bograd & Ono 2013).

The high mean concentration values observed for nitrate-NO_3^- and phosphate-PO_4^{3-} in AAIW were also observed in other studies that analyzed these parameters (Azar et al. 2021; Panassa et al. 2018; Stramma & Schmidtko 2020). This high nutrient concentration in AAIW is a response to its region of formation, in the Atlantic sector of the Southern Ocean, which corresponds to a large high-nutrient low-chlorophyll (HNLC) region. The nutrients are supplied from below through upwelling process (Peterson & Whitworth 1989; Talley 1996) and remain mainly unused in the surface due to the iron and light limitation (De Baar et al. 1997; Mitchell et al. 1991; Nelson & Smith 1991). Thus, most of these nitrate-NO_3^- and phosphate-PO_4^{3-} subduct during the AAIW formation, enriching the water mass (Peterson & Whitworth 1989; Talley 1996). After that, these high nutrients concentration flow northwards and enhance the biological response and export production in the equatorial upwelling (Marinov et al. 2006).

According to the section figures of phosphate-PO_4^{3-} and nitrate-NO_3^- vertical distribution in AAIW in the GLODAPv.2 35°W section (Figures 5A and 5B), it is possible to notice that the distribution of these nutrients is parabolic, indicating that nutrient concentrations are lower at the edges of the water mass and higher at its center. This distribution pattern indicates that the water mass suffers a mixing process at its edges, changing the concentration of nutrients in this regions (Mamayev 1975; Talley 1996).

In the WTAO the parabolic nutrient pattern in the AAIW could be a result of the dynamic system along north-east Brazil's margin and the tropical region. Off the Brazilian margin, AAIW is transported by the Intermediate Western

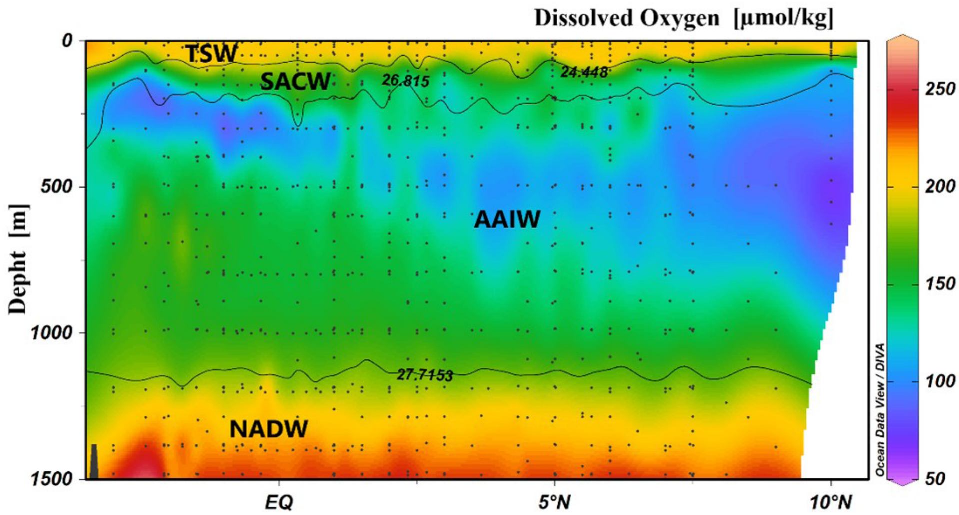

Figure 6 Vertical profile for dissolved oxygen (µmol kg–1), along the 35°W transect for GLODAPv.2 from the surface to 1500 m, between 3°S and 11°N (1990 – 2010). The gray dots represent the sampling depths. The acronyms correspond to: TSW – Tropical Surface Water; SACW – South Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water.

Boundary Current (IWBC) northwards and some wedges of this current spread eastward between 05°S and 10°N, returning to the west following the circulation pattern. In these Equatorial wedges, the salinity suffers an erosion process at the edges through horizontal and vertical mixing, since there the shear is stronger (Schmid & Garzoli 2009). Considering that the salinity suffers an intense mixing process, it would also be expected that other parameters, such as nitrate-NO_3^- and phosphate-PO_4^{3-}, also suffer this mixing.

It was possible to notice that both nitrate-NO_3^- and phosphate-PO_4^{3-} have a very characteristic range of variation in AAIW, which can be used to differentiate it from adjacent water masses. On the other hand, silicic acid-Si(OH)4 does not have a specific concentration in this water mass that differentiates it from the overlying and underlying ones, not making it a good tracer.

4.4 North Atlantic Deep Water

NADW was observed between 1300 and 4000 m and can be easily differentiated from its adjacent water masses due to its lower nitrate-NO_3^- and phosphate-PO_4^{3-} concentrations (Supplementary Table S3). Nitrate-NO_3^- showed constant and continuous concentrations in PIRATA XVII and in the GLODAPv.2 (Figures 3A and 5A), with a mean value of 20 µmol/kg, occasionally increasing up to 30 µmol/kg.

Phosphate-PO_4^{3-} also showed a continuous and constant distribution pattern throughout the entire NADW for the two campaigns and GLODAPv.2 (Figures 3B and 5B). The difference between the PIRATA campaigns and GLODAPv.2 data is that the PIRATA campaigns have a few isolated points where the concentration is higher than those at GLODAPv.2. Thus, the results observed in this study were also observed by Kawase & Sarmiento (1985) who found that NADW is characterized by a decrease in nutrient contents in relation to the adjacent water masses. These authors also mentioned that this distribution pattern in NADW coincides with a relative increase in dissolved oxygen (Figure 2) concentrations.

In the PIRATA XVIII campaign, NADW showed silicic acid-$Si(OH)_4$ concentrations in a range that ranged between 5 – 30 µmol kg^{-1} (Figure 4C; Supplementary Table S3). On the other hand, PIRATA XVII and GLODAPv.2 showed more similarities (Supplementary Table S2) and shared a more extensive concentration range (15 – 60 µmol kg^{-1}) (Supplementary Table S3). According to silicic acid-$Si(OH)_4$ section from GLODAPv.2 (Figure 5C), it is possible to see three different layers with different concentration ranges in NADW. In the upper portion (~ 1300 – 2000 m), silicic acid-$Si(OH)_4$ concentration varies between 10 and 20 µmol kg^{-1}; in the middle (~ 2000 – 3000 m), silicic acid-$Si(OH)_4$ varies between 20 and 30 µmol/kg; while in the lower one (~ 3000 – 4000 m), the variation occurs between 30 and 45 µmol kg^{-1}.

These three different layers in NADW could be associated with the concept of lower, middle and upper NADW used in the literature and demonstrated by Herrford, Brandt & Zenk (2017). In this context, the upper, middle and lower components of the NADW would have gone through different formation processes in different regions, being the

Mediterranean Sea (Arhan et al. 1998), the eastern part of Iceland, and the Danish Strait (Dickson & Brown 1994), respectively. These results also suggests that in the WTAO the source waters that compose NADW can be differentiated in the basis of silicic acid-$Si(OH)_4$ concentration ranges, in agreement with the Optimum Multi-Parameter analysis performed by Ferreira & Kerr (2017). The use of semi-conservative parameters such as silicic acid-$Si(OH)_4$ could be considered as a tool to track regional transitioning from the lower NADW to the upper AABW (Herrford, Brandt & Zenk 2017).

4.5 Antarctic Bottom Water

AABW was observed below 4000 m in the WTAO, only south of the Mid-Atlantic Ridge (from 03°S to approximately 10°N) and presents considerably high nitrate-NO_3^- and phosphate-PO_4^{3-} concentrations, with approximately 30 and 2 µmol/kg, respectively (Figures 3A, 3B, 4A, 4B, 5A and 5B), making these two nutrients good tracers for the AABW, as the NADW has lower nitrate-NO_3^- and phosphate-PO_4^{3-} concentrations.

However, silicic acid-$Si(OH)_4$ is the best biogeochemical tracer for characterizing the AABW, since the mean concentration of this nutrient in this water mass is higher than the above-lying NADW. Mean silicic acid-$Si(OH)_4$ concentration in the AABW varies between 50 and 100 µmol/kg, with its nucleus being around 100 µmol/kg (Figures 3C, 4C and 5C; Supplementary Table S3). According to Boswell et al. (2002), the AABW dissolved silicic acid-$Si(OH)_4$ enrichment originates from the dissolution of diatom frustules, which after death sink and accumulate in the sediment (Tréguer et al. 1995). The biogenic silica is then converted into dissolved inorganic silicon (silicic acid-$Si(OH)_4$), thus increasing the concentrations of this nutrient in the deep waters of the Southern Ocean through diagenetic release (Boswell et al. 2002).

It is also important to document the nutrients and dissolved oxygen concentrations in both NADW and AABW because of the warming trends of $2.5 \pm 0.7 \cdot 10^{-3}$ °C yr^{-1} in the northern Brazil Basin (Herrford, Brandt & Zenk 2017). The authors also state that this regional warming trend cannot be attributed only to the weakening of the abyssal circulation, but to other processes such as a greater contribution of the Circumpolar Deep Water to the AABW in the Southern Ocean.

5 Conclusion

As previously described by many authors, using dissolved nutrient data proved to be a promising tool to investigate whether these non-conservative parameters could further improve water mass characterization in the WTAO. According to the datasets from the 2017 and 2018 PIRATA campaigns and the GLODAPv.2.2020, it was possible to see that the biogeochemical parameters nitrate-NO_3^-, phosphate-PO_4^{3-}, and silicic acid-$Si(OH)_4$ can be used as an additional tool to the characterization of water masses, since specific concentration ranges of nutrients within the water masses were observed. TSW is a water mass that can be identified by the very low nutrient concentrations (or even below the method detection limit). SACW had nitrate-NO_3^- and phosphate-PO_4^{3-} concentrations higher than TSW, but much lower than AAIW, being possible to differentiate this water mass by this intermediate range. NACW also presented intermediate concentrations between the adjacent water masses, and nutrient concentrations very similar to SACW, but a little lower in general, which suggests some influence of the northeastern tropical Atlantic OMZ in the WTAO region. AAIW was the water mass that showed the highest concentrations of phosphate-PO_4^{3-} and nitrate-NO_3^-, and it can be straightforwardly characterized by these nutrients in addition to the conservative parameters. High silicic acid-$Si(OH)_4$ concentrations characterize AABW, although phosphate-PO_4^{3-} and nitrate-NO_3^- also have a different signature in AABW when compared to NADW, which has lower concentrations of these nutrients.

Finally, this water mass characterization study is a contribution to understanding the biogeochemical features; the availability of other parameters than θ-S allows the application of tools such as the Optimum Multi-Parameter analysis to better identify the source waters to local water masses. It is expected that this study may contribute to future regional water masses studies in view of understanding temporal variability and trends for their physical and biogeochemical properties in a changing ocean.

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7 Supplementary Material

The following online material is available for this article:

Table S1: Normality p-values for the PIRATA databases. In white: Normally distributed data; in grey: data with non-normal distribution. TSW – Surface Tropical Water; SACW – South Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water; AABW – Antarctic Bottom Water.

Table S2: p-values for Dunn's comparative statistical test (pairwise), after Kruskal-Wallis analysis, for TSW, SACW, AAIW, NADW and AABW water masses. Also p-values for Wilcoxon-Mann-Whitney test for NACW and for the nitrate parameter only in SACW (marked with *). In white: datasets do not differ significantly; in grey: datasets differ significantly. TSW – Surface Tropical Water; SACW – South Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water; AABW – Antarctic Bottom Water.

Table S3: Mean, minimum, maximum and standard deviation values of the main physical-chemical parameters related to this work. In the PIRATA dataset, potential temperature, salinity and potential density data were acquired through the CTD-O_2 system, while nitrate, nitrite, phosphate, silicate and O_2 data were obtained in the laboratory through the analysis of discrete samples collected with Niskin bottles. TSW – Surface Tropical Water; SACW – South Atlantic Central Water; AAIW – Antarctic Intermediate Water; NADW – North Atlantic Deep Water; AABW – Antarctic Bottom Water.

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Author contributions

Renan Luis Evangelista Vieira: conceptualization; formal analysis; methodology; validation; writing-original draft; writing – review and editing; supervision; visualization; sampling onboard, laboratory analysis. **Leticia Cotrim da Cunha:** conceptualization; formal analysis; methodology; validation; writing – review and editing; funding acquisition; supervision; visualization; sampling onboard, laboratory analysis. **Luana Queiroz Pinho:** methodology; validation; writing – review and editing. **Alexandre Macedo Fernandes:** methodology; validation; writing – review and editing. **Raquel Avelina da Conceição dos Santos:** writing – review and editing; sampling onboard, laboratory analysis. **Ricardo de Almeida Keim:** supervision; sampling onboard, laboratory analysis. **Carlos Augusto Musetti de Assis:** formal analysis; writing – review and editing; sampling onboard, laboratory analysis. **Thiago Veloso Franklin:** sampling onboard, laboratory analysis. **Jessica da Silva Nogueira:** sampling onboard, laboratory analysis.

Conflict of interest

The authors declare no potential conflict of interest.

Data availability statement

All data included in this study are available on request.

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