Ocean acidification studies and the uncertainties relevance on measurements of marine carbonate system properties

Adriana Rodrigues Perretti[1,5], Ana Cecília Rizzatti de Albergaria-Barbosa[2,5], Rodrigo Kerr[3,5], Leticia Cotrim da Cunha[4,5]*

[1] Centro de Estudo do Mar da Universidade Federal do Paraná - UFPR
(Av. Beira-mar, s/n. Caixa Postal: 61 - Pontal do Paraná - PR - 83255-000 - Brazil)
[2] Instituto de Geociências da Universidade Federal da Bahia - UFBA
(Rua Barão de Jeremoabo, s/n - Ondina - Salvador - BA - 40170-115 - Brazil)
[3] Instituto de Oceanografia da Universidade Federal do Rio Grande - FURG
(Av. Itália, km 8 - Bairro Carreiros - Rio Grande - RS - 96203-900 - Brazil)
[4] Faculdade de Oceanografia do Estado do Rio de Janeiro - UERJ
(Rua São Francisco Xavier, 524 - Rio de Janeiro - RJ - 20550-900 - Brazil)
[5] Brazilian Ocean Acidification Network
(BrOA - www.broa.furg.br, broa@furg.br) (Rio Grande - RS - 96203-900 - Brazil)

*Corresponding author: adriana.perretti@ufpr.br

The global ocean has a key role on the Earth's climate system. It possesses a direct connection with the atmospheric gases, including the greenhouses, allowing exchanges between those compartments and oceanic storage of carbon. Through the years, this exchange of gases occurred based on gas equilibrium between ocean and atmosphere. After the Industrial Revolution, human activities have increased the emissions of greenhouse gases, mainly carbon dioxide (CO_2), which changed the atmospheric concentration from ~280 ppm of CO_2 to values as high as 391 ppm between c.a. 1750 and 2011 (Ciais et al., 2013). Recently, the measured CO_2 atmospheric values are ranging near or above 400 ppm, as recorded by the Mauna Loa observatory, in Hawaii (daily CO_2 measurements information available on www.scripps.ucsd.edu). A regional study in the south-southeast Brazilian continental shelf agrees with this value, which has measured an average of 396.7±2.5 ppm in the atmosphere during the spring of October 2014 (Kerr et al., 2016). This enhancement is reflected in the ocean, which has absorbed about 25% to 30% of the anthropogenic atmospheric CO_2 emissions (Sabine and Tanhua, 2010; Le Quére et al., 2016). The CO_2 uptake by the oceans directly affects the seawater chemistry and marine biogeochemical processes, impacting both the ecosystems and their respective biota (Doney et al., 2009).

Atmospheric CO_2 can be transferred to seawater through the air-sea interface, where it dissolves and reacts with H_2O forming the carbonic acid (H_2CO_3). The H_2CO_3 is a weak acid and promptly suffers two dissociation processes that release protons (H^+): the first one originates bicarbonate ion (HCO_3^-); and the second one, carbonate ion (CO_3^{2-}) (Figure 1). The term total dissolved inorganic carbon (DIC) is the sum of the three main inorganic forms of CO_2 in seawater (i.e., CO_2*, HCO_3^- and CO_3^{2-}; the CO_2* represents the sum of $CO_{2(aq)}$ and H_2CO_3 because the latter is rapidly dissociated in seawater), which can be also referred, in some works, as C_T, TIC, TCO_2 or $\sum CO_2$ (Zeebe, 2012). The equilibrium system of the DIC species on seawater is known as the marine carbonate system and is the main responsible to drive the buffer capacity of the ocean. Thus, the chemical species of the carbonate system in seawater changes to equilibrate the H^+ content, leaving the ocean with an average pH around 8.2 units (Zeebe and Wolf-Gladrow, 2001).

The intensification on the amount of CO_2 in the atmosphere enhances the dissolution of this gas in the seawater, changing the pH of the oceans. The decrease of ocean pH due to the anthropogenic CO_2 uptake is known as *ocean acidification* (OA), also presented as "the other CO_2 problem" (Doney et al., 2009). Due to the current increase rate in atmospheric CO_2 concentration, the mean pH on the surface waters has already decreased by 0.1 units since 1750 (Bindoff et al., 2007). In general, this 0.1 units decrease in pH could be considered a small and irrelevant change, however, this equals to 30% increase on the H^+ content in seawater, as pH corresponds to the inverse logarithm of H^+ ions activity. Moreover, with the continuous increase on the atmospheric CO_2, it is predicted a decline in pH of around 0.3-0.4 units until 2100 (Meehl et al., 2007). The actual and predicted pH decrease will affect the ocean environment and its resources, impacting not only its biodiversity, but also food security and

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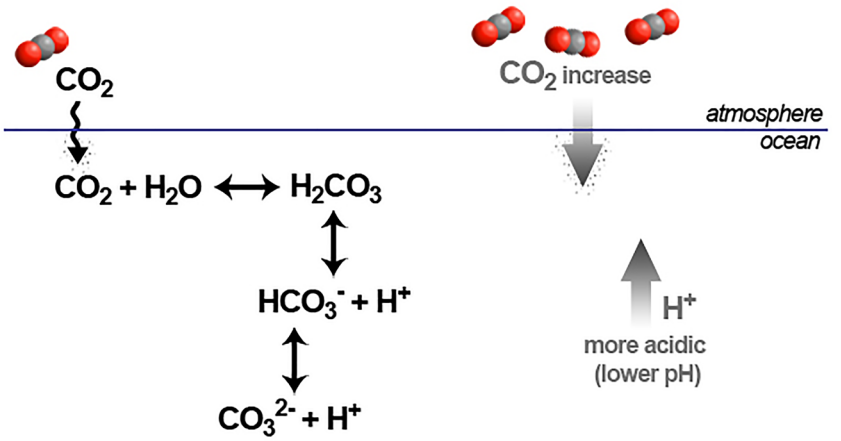

Figure 1. Marine carbonate system basic equilibrium. Schematic representation of the CO_2 air-sea exchange and the basic equilibriums of the marine carbonate system in seawater.

economy of countries that rely on fisheries and aquaculture as an important source of income. Thus, it is essential to understand the perturbation of the pH change on the ocean and its several consequences.

The first OA studies have discussed mainly the changes in seawater biogeochemistry, followed by studies on the OA effects on different organisms (especially those with a calcium carbonate structure) and environments (e.g. Orr et al., 2005; Feely et al., 2004; Caldeira and Wickett, 2003; Kleypas et al., 1999; Brewer, 1997; Haugan and Drange, 1996; Broecker et al., 1979). However, despite the OA research increase on the first decades of the 21th century, there are some issues that remain unsolved (e.g. Browman, 2016; Yang et al., 2016), like the OA effects in organisms, ranging from negative to neutral (and even positive), and the multiple stressors studies difficulty, due to the combination of the several drivers as oxygen and temperature (Browman, 2016). It is also important to emphasize in OA studies the different responses that each ecosystem types may display in case of changes. For example, coastal shallow water areas will likely have their carbonate system strongly affected by changes in the biological processes like photosynthesis and remineralization (e.g. Waldbusser and Salisbury, 2014; Duarte et al., 2013; Andersson and Mackenzie, 2012; Feely et al., 2010).

The significant increase in the number of studies targeting OA has led to further thinking on the rapidly growing field of research (Riebesel and Gattuso, 2014), with the identification of the highest priorities for future investigations on the changing ocean (Newton et al., 2015). These goals are: (i) improve our understanding of the actual global OA state; (ii) improve our understanding of the ecosystem changes under the OA pressure; (iii) improve the models related to the OA and its impacts. Furthermore, the fast increase in the number of OA papers brought up some concerns about the data generated on these studies, one of them being data quality, which is direct related to the measurements precision (Newton et al., 2015). It is important to note that, analytically, the precision is related to the measurement repeatability, while the accuracy corresponds to the difference between a measurement and a "true" value. On this note, we follow the uncertainty definition by Newton et al. (2015), i.e. "it is the mean standard uncertainty of measurement, which that is with the associated confidence interval equivalent to that for a standard deviation".

Distinct purposes of research need to achieve different measurement quality goals. Studies regarding multi-decadal time-series changes in an open ocean station will deal with a "signal to noise" relationship different from that observed in an estuarine system study (Newton et al., 2015). According to this requirement, the Global Ocean Acidification Observing Network (GOA-ON; www.goa-on.org) has defined two quality criteria to be used in OA studies: *weather* and *climate* data; both defined in Newton et al. (2015). It is interesting to emphasize that these criteria are not related to the climatic science, despite their names, but are only a way to distinguish the quality of the acquired carbonate system data (e.g. Bockmon and Dickson, 2015).

Weather data are those of "sufficient quality to identify relative spatial patterns and short-term variation", which supports interpretation of ecosystem response in dynamic studies. *Climate* data are those with "quality sufficient to assess long-term trends with a defined level of confidence", which is related to low dynamic studies, like changes in the hydrographic conditions in long-term studies. Thus, in a hypothetical case where it is necessary to obtain the CO_3^{2-} concentration, one will need to have an uncertainty of 10% for *weather* data and 1% to *climate* data (Newton et al., 2015). However, despite of the data type, all results should be accompanied by: (i) the uncertainty of the obtained data (measured or estimated), (ii) the standard material and the equilibrium constants applied, and (iii) the units and scales. These results, *weather* or *climate*, can be submitted to the global databases, allowing knowledge improvement and comparison of the carbonate system variables processes. It is important to highlight that all studies also need to present four basic parameters: temperature, salinity, pressure (or water depth) and dissolved oxygen concentration, which are essential ocean variables. Fluorescence and irradiance are also important parameters and should be presented when available, since they may serve as primary production proxies (biological activity affects the carbonate system; Newton et al., 2015).

In general, studies concerning OA and the marine carbonate system usually evaluate only two of the six main variables to estimate the whole carbonate system parameters. This approach is known as "two out of six" strategy (Zeebe, 2012). This method is based in the fact that the whole carbonate system can be described by six main variables:DIC, total alkalinity (TA), $[CO_2^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$ and $[H^+]$. To the purposes of this note we will consider a simplified view of the variable TA, a measure of the difference between proton donors and acceptors in seawater, as presented by Zeebe (2012) (Equation 1). This simplification does not specify the minor components that can affect TA. These components are ions like NH_4^+, NO_3^-, HPO_4^{2-} or $H_3SiO_4^-$, which alter TA particularly in coastal and estuarine areas due to processes as denitrification and organic matter remineralization (Wolf-Gladrow et al., 2007).

All the six main carbonate system variables (DIC, TA, $[CO_2^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$ and $[H^+]$) are in thermodynamic equilibrium and have known constants, which convey in a set of four equations and six unknown variables (Zeebe, 2012). Thus, if two variables of the system are known, like pH ($[H^+]$) and DIC, the four equations can be solved to estimate the four unknown variables. To estimate the unknown variables of the carbonate system it is possible to use several specific open-source software packages (Orr et al., 2015). This approach encourages the study of the carbonate system, because it is not necessary to analytically determine each system variable. Moreover, the efforts to achieve quality measurements can be focused in only two variables.

$$TA \approx [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + [minor\ components] \quad (1)$$

The choice of the two variables to be analyzed will depend on the carbonate system parameters of interest on the study and on the analytical capacity of the laboratory (e.g. Bockmon and Dickson, 2015). The laboratory capability will rely on its competence to follow the recommended methods (Riebesell et al., 2011; Dickson et al., 2007; DOE, 1994) or, when using alternative methods, the evaluation of its reproducibility and accuracy according to international standards (Bockmon and Dickson, 2015). It is important to understand that the two variables chosen to estimate the unknown variable will directly affect the uncertainty attached to it (e.g. Millero, 2007). For example, pairing pH and TA to estimate $[CO_3^{2-}]$ leads to an uncertainty around 3.7%, while when using DIC and TA it will be around 1.7% (based on the common uncertainty of the state of the art methodologies) (Dickson, 2011). Moreover, the techniques available to determine the marine carbonate system variables have different uncertainties attached to them. For example, the common techniques to determine pH on OA studies have uncertainties ranging from 0.003 to 0.01 pH units (spectrophotometric determination using m-cresol purple and potentiometric determination with standard Tris, respectively; both with certified reference material (CRM) calibration), while for TA it ranges from 1.2 to 10 µmol kg^{-1} (closed and open cell titration, respectively; both with CRM calibration) (Dickson, 2011). The effect of these differences on the estimation of a variable like $[CO_3^{2-}]$ can change its final uncertainty to around 2% (Figure 2). However, it is important to emphasize that, on this example, the effect of the pH uncertainty on the $[CO_3^{2-}]$ estimation is stronger when compared to TA, as observed in Figure 2. Therefore, the choice of the variables that will be analyzed rely not only on the technical capability of the laboratory, including the sampling procedure, but also on the uncertainty that you need for the estimation of carbonate system variables. The final uncertainty of the carbonate

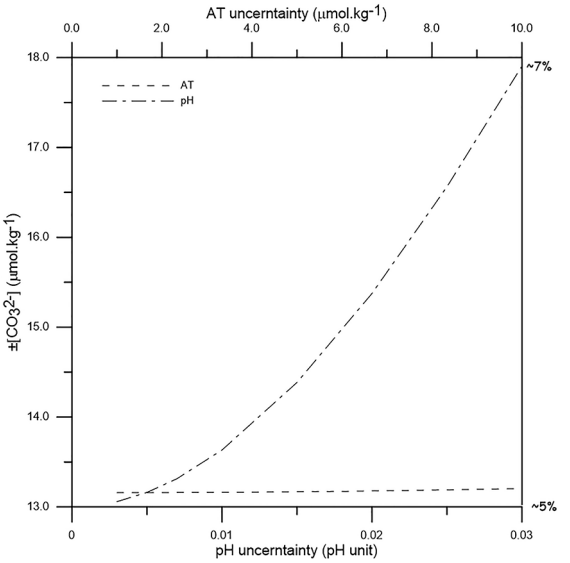

Figure 2. Final uncertainties differences according to carbonate parameters uncertainties. Changes on the estimated [CO_3^{2-}] final uncertainty according to different pH and AT uncertainties (based on the values presented in Dickson, 2011). Calculated using CO2sys v2.2 and the hypothetical values: S = 35, T = 20ºC, [phosphate] = 2 µmol kg^{-1}, [silicate] = 60 µmol kg^{-1}, TA = 2300 µmol kg^{-1}, pH = 8.2, with estimated [CO_3^{2-}] = 241 µmol kg^{-1}. The scales and constants chosen on software were: total pH scale; K1 and K2 from Lueker et al. (2000); KS from Dickson (1990) and KB from Uppström (1974). The uncertainties in constants applied to the software were: 0.004 for pK0; 0.015 for pK1; 0.03 for pK2; 0.01 for pKb; 0.01 for pKw; 0.02 for pKsp aragonite and 0.02 for pKsp calcite (the choice of these values is based on personal communication to Orr, J.C.).

system estimated variables can be achieved using the error propagation technique (Gattuso et al., 2016).

The acceptable uncertainty on each study, *climate* or *weather* (Table 1), will depend on the purposes of each research. Long term studies in the open ocean surface, for example, have very small changes on pH through time, thus any slight variability needs to be precisely obtained. Therefore, when the variability of a parameter is restrained, it is necessary to achieve the lowest uncertainty possible (e.g., for a pH change of 0.005 units the uncertainty should be < 0.005). In comparison, in eutrophic estuarine systems the pH may change several units within the tidal cycle (values ranging in general between 7 to 8 pH units with the sea front entering/leaving the system), which allows the use of higher uncertainty techniques (e.g., for a pH change of 0.05 units the uncertainty could be > 0.005, but not < 0.05). It is important to emphasize that the values presented on Table 1 need to be considered carefully and as a guide. According to Bockmon and Dickson (2015), very few laboratories can achieve the *climate* uncertainties of Table 1 and could be worthwhile that the OA community review the acceptable uncertainties to each goal. For example, in an inter-laboratory comparison more than half laboratories achieved a TA uncertainty of 5 μmol kg^{-1} (Bockmon and Dickson, 2015) which is similar to the *climate* order of magnitude; however, according to Table 1 it still characterized as a *weather* data.

Recent initiatives are working to organize both regionally and globally the scientific community, to improve the compilation of data and the technical capacity. The GOA-ON initiative emphasizes the development of carbon observation networks in the international community, establishing methods and standards to be used by researchers. In Latin America, scientists from seven countries, including Brazil, established the Latin-American Ocean Acidification Network (LAOCA, www.laoca.cl) in 2015. Among the goals of LAOCA, it is important to highlight that: (i) standard analytical techniques need to be defined, enhancing quality data; and (ii) the commitment between the network members to make their results available in a database after two years from the end of the study.

The OA community is rapidly increasing in Brazil (Brazilian Ocean Acidification Network - BrOA; www.broa.furg.br), with studies from different research areas covering different parts of the Brazilian coastline, the open ocean areas and the western South Atlantic Ocean (*e.g.* Longuini et al., 2015; Cotovicz et al. 2016a; Kerr et al., 2016; Ito et al., 2016; Lencina-Avila et al., 2016; Orselli et al., 2018) and the Southern Ocean (*e.g.* Kerr et al., 2018a, 2018b; Lencina-Avila et al., 2018) (Table 2). The relevant increase in Brazilian OA publications in the last years emphasizes the importance of applying and publishing the estimation of uncertainties for the marine carbonate system variables, allowing the national research to achieve international quality standards and to contribute to global ocean databases such as SOCAT (Bakker et al., 2016) and GLODAP (Olsen et al., 2016). Thus, not only improving the knowledge concerning the OA, but also increasing the visibility of Brazil in the international scientific community. It is evident, according to the last BrOA Network publication (Kerr et al., 2016), that the Brazilian OA community is improving the data quality and technical information, even considering the distinct approaches and ecosystems, which includes: evaluation of carbonate system parameters and/or acidification in rivers (Abril et al., 2014), estuaries (Cotovicz et al., 2015; Cotovicz et al. 2016b), lagoons (Peixoto et al., 2013), lakes (Marotta et al., 2014; Fontes et al., 2015) and open ocean

Table 1. The uncertainties of the standard carbonate system parameters for each data quality goal, *weather* or *climate*, according to Newton et al. (2015).

	Quality goals data	
	weather	*climate**
$[CO_3^{2-}]$	10 %	1 %
pH	0.02 units	0.003 units
TA	10 µmol kg^{-1}	2 µmol kg^{-1}
DIC	10 µmol kg^{-1}	2 µmol kg^{-1}
pCO_2	2.5 %	0.5 %

* the level of precision required is only achievable by limited laboratories and usually for some of the variables described here.

Table 2. Examples of marine carbonate system and OA studies executed by Brazilian research groups since the BrOA Network creation in 2012. The analyzed parameters, the weather/climate classification based on the precision of measurements, and the indication of use of certified reference materials (CRMs, as recommended in Dickson et al. 2007) are included. Figure 3 shows the geographical location of each study. Other studies can be accessed at www.broa.furg.br.

Reference nº.	Reference	Study area	Analyzed parameters (precision)	Quality level [a]	Use of CRMs
1	Bonou et al. (2016) [b]	Tropical Atlantic	DIC (±1.64 - 2 µmol kg^{-1}) TA (±0.03 - 2.39 µmol kg^{-1})	Climate	Yes
2	Bruto et al. (2017)	NW Tropical Atlantic	fCO_2 (±3 µatm)	Climate	CARIOCA sensor
3	Cotovicz Jr et al. (2015)	SE Brazil	pCO_2 (±3.0 ppmv) TA (±3 µmol kg^{-1}) pH (±0.01)	Climate/ Weather	Yes
4	Cotovicz Jr et al. (2016b)	SE and NE Brazil	TA (±3 µmol kg^{-1}) pCO_2 (±3.0 ppmv) pH (±0.01)	Climate/ Weather	Yes
5	Guenther et al. (2017)	NE Brazil	pH (±0.005) TA (±10 µmol kg^{-1})	Weather*	No
6	Ito et al. (2016)	SW South Atlantic	pCO_2 seawater (±0.3 µatm) pCO_2 air (±0.1 µatm)	Climate	No
7	Kerr et al. (2018a)	Southern Ocean	DIC (±5 µmol kg^{-1}) TA (±3 µmol kg^{-1})	Weather*	Yes
8	Kerr et al. (2018b)	Southern Ocean	DIC (±5 µmol kg^{-1}) TA (±3 µmol kg^{-1})	Weather*	Yes
9	Lencina-Avila et al. (2016)	South Atlantic	pCO_2 (±0.6- 0.9%)	Climate	Yes
10	Lencina-Avila et al. (2018) [c]	Southern Ocean	TA (ranging from not informed to ±4.4 µmol kg^{-1}) DIC (ranging from 2.7 to ±5.6 µmol kg^{-1})	Climate /Weather*	Yes
11	Longhini et al. (2015)	NE Brazil	pH (±0.01) TA (±5 µM)	Weather*	Yes
12	Noriega & Araujo (2014)	N and NE Brazil - estuaries	pH (±0.005) TA (±20 µmol kg^{-1})	Weather*	No
13	Noriega et al. (2015)	NE Brazil - estuaries	pH (±0.005) TA (±20 µmol kg^{-1})	Weather*	No
14	Orselli et al. (2018)	SW Atlantic	DIC (±4.0 µmol kg^{-1}) TA (±2.3 µmol kg^{-1})	Climate/ Weather*	Yes

[a] The quality level on this Table was defined according to Table 1. The character * indicates the data that is closer to *climate* than *weather* goal, but still characterized as *weather*.

[b] Bonou et al. (2016) used an historical dataset from 35 available cruises executed in the Western Tropical Atlantic from 1989 to 2014. So, distinct methods with distinct precisions were used.

[c] Lencina-Avila et al. (2018) reconstructed the carbonate system parameters from hydrographic data obtained in the study region (e.g. Mata and Kerr, 2016a, 2016b; Azaneu et al., 2013; Dotto et al., 2016; Kerr et al., 2018a, 2018b; Lencina-Avila et al., under review). The marine carbonate system parameters were measured for years 2015 and 2016.

areas (Ito et al., 2016; Orselli et al., 2018); studies of the impact of OA and other stressors in marine biota (Garrard et al., 2013; Rodríguez-Romero et al., 2014; Goulding et al. 2017); and laboratory experiments (Orte et al., 2014; Scherner, et al., 2016; Schneider et al., 2018). Some examples of the BrOA studies done in the last five years associated with their classification based on the method precision are summarized in Table 2 and Figure 3. The members of BrOA Network have also been involved in OA best practices measurements discussions and workshops, increasing the number of researchers committed to the dissemination and use of best analytical practices to determine the parameters of the marine carbonate system. This is important to place the Brazilian OA studies in an international scenario, as well as to fill a gap of unknown information about the Tropical and South Atlantic OA oceanographic processes with a desirable quality.

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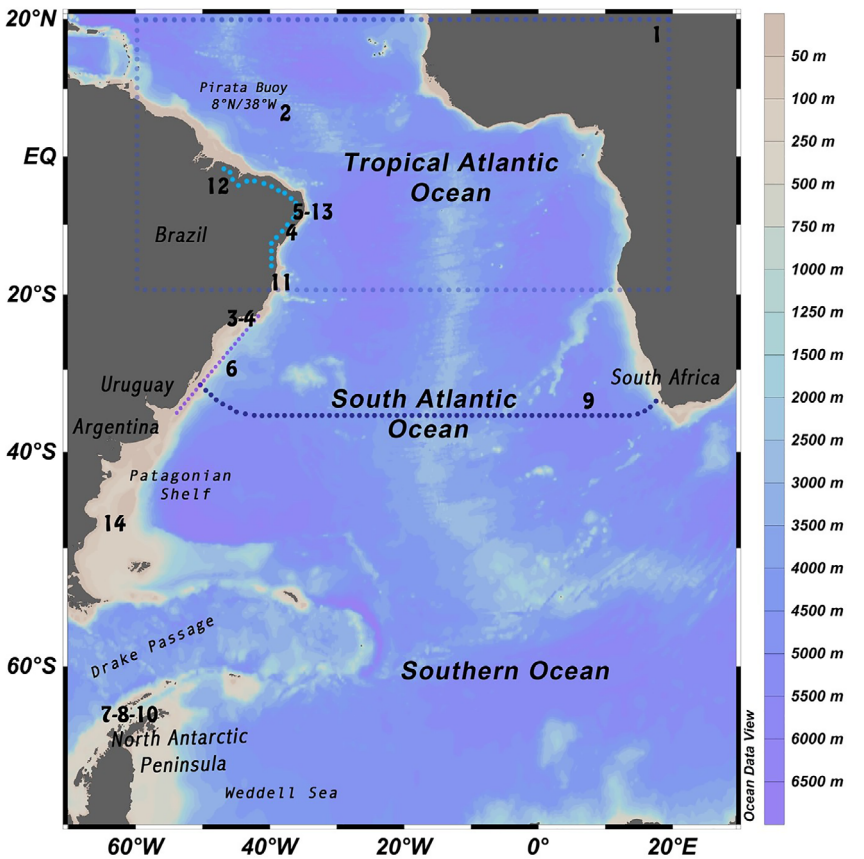

Figure 3. Map indicating the study area of the works from Table 2. Map of the tropical and south Atlantic, including the Atlantic sector of the Southern Ocean. The numbers indicate the references cited in the table 2. The different dotted lines delimit study areas or transects of the references. Light blue: Bonou et al. (2016); blue: Noriega & Araujo (2014); dark blue: Lencina-Avila et al. (2016); purple: Ito et al. (2016).

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