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Characterization of ocean biogeochemical processes: a generalized total least-squares estimator of the Redfield ratios

V. Guglielmi^{1,2}, C. Goyet^{1,2}, and F. Touratier^{1,2}

¹Images Espace-Dev, University of Perpignan 52, Avenue P. Alduy, 66860 Perpignan, France

²Espace-Dev UMR UG UA UM IRD, Maison de la télédétection, 500 rue J.-F. Breton, 34093 Montpellier, France

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Correspondence to: V. Guglielmi (veronique.guglielmi@univ-perp.fr)

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Abstract

The chemical composition of the global ocean is governed by biological, chemical and physical processes. These processes interact with each other so that the concentrations of carbon dioxide, oxygen, nitrate and phosphate vary in constant proportions, referred to as the Redfield ratios. We build here the Generalized Total Least-Squares estimator of these ratios. The interest of our approach is twofold: it respects the hydrological characteristics of the studied areas, and it can be applied identically in any area where enough data are available. The tests performed on the Atlantic Ocean highlight a variability of the Redfield ratios, both with geographical location and with depth. This variability emphasizes the importance of local and accurate estimates of Redfield ratios.

1 Introduction

Most of the elements and the terrestrial chemical compounds (including atmospheric gases) are soluble in the ocean. In the upper ocean, there is a layer called the “mixed layer” because this layer is submitted to movements of turbulence and convection. Its thickness varies from a few tens of meters in summer when surface waters are warm, to several hundred meters in winter when surface waters cool and are moved by violent winds. In 1934, Redfield (1934) was the first to observe that below this mixed layer, the concentrations of carbon dioxide, oxygen, nitrate and phosphate vary in constant proportions, called “Redfield ratios” since.

The commonly admitted explanation for this phenomenon is related to the biological activity of marine microorganisms. Carbon enters into the constitution of every living being, but nitrate (NO_3^-) and phosphate (PO_4^{3-}) are also essential nutrients. At the ocean surface, in the area that receives light, phytoplankton uses the sun’s energy to grow. It is photosynthesis, which produces oxygen and transforms carbon dioxide dissolved in seawater, nitrate and phosphate into organic carbon. The reverse reaction is

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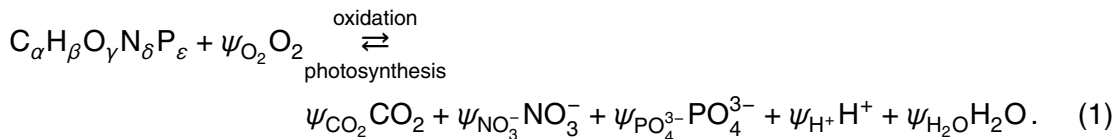
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the oxidation of organic matter, or remineralization, which includes the respiration of organisms and, when they die, their decomposition. Below the mixed layer, this oxidation is solely responsible for variations in concentrations of carbon dioxide, oxygen, nitrate and phosphate. That these variations remain in constant ratios means simply that the biological activity follows the same rules everywhere in the ocean.

This is represented by the following chemical reaction:



$C_{\alpha}H_{\beta}O_{\gamma}N_{\delta}P_{\varepsilon}$ is a fictitious molecule, which contains the elements entering into the composition of any organic matter. The coefficients α , β , γ , δ , ε are determined by the different stoichiometric coefficients of the reaction: ψ_{O_2} , ψ_{CO_2} , $\psi_{NO_3^-}$, $\psi_{PO_4^{3-}}$, ψ_{H^+} and ψ_{H_2O} .

The Redfield ratios are the ratios of these stoichiometric coefficients. Let us take the example of the concentrations of oxygen and nitrate. When the oxygen concentration decreases by ΔO_2 , the concentration of nitrate increases by: $\Delta NO_3^- = \frac{\psi_{NO_3^-}}{\psi_{O_2}} \Delta O_2$. These concentrations therefore vary according to a constant ratio, called R_{ON} and defined by:

$$R_{ON} = \frac{\Delta O_2}{\Delta NO_3^-} = \frac{\psi_{O_2}}{\psi_{NO_3^-}}. \quad (2)$$

Similarly, we define the coefficient R_{OP} :

$$R_{OP} = \frac{\Delta O_2}{\Delta PO_4^{3-}} = \frac{\psi_{O_2}}{\psi_{PO_4^{3-}}} \quad (3)$$

and the coefficient R_{NP} , which can be deduced from the two previous ones:

$$R_{NP} = \frac{\Delta \text{NO}_3^-}{\Delta \text{PO}_4^{3-}} = \frac{\psi_{\text{NO}_3^-}}{\psi_{\text{PO}_4^{3-}}} = \frac{R_{OP}}{R_{ON}}. \quad (4)$$

The Redfield's concept therefore asserts the existence of coefficients R_{ON} , R_{OP} , and R_{NP} which are constant, both with time and with space.

Determining the values of these coefficients is of great interest, especially nowadays.

5 These coefficients are involved not only in the nutrients cycle but also in the carbon cycle (Goyet and Brewer, 1993; Roy-Barman and Jeandel, 2011). On the ocean surface, the atmospheric carbon dioxide dissolves in seawater; in surface waters, photosynthesis consumes carbon dioxide and transforms it into organic carbon; carbon is released into deeper waters by the oxidation of organic matter. This is the biological carbon
10 “pump”.

Actually, human activities cause a dramatic increase of carbon dioxide into the atmosphere. So the ocean absorbs more and more carbon dioxide, which brings about unprecedented changes in ocean biogeochemical processes and in marine ecosystems. To know how the biological activity continues to drive the carbon dioxide, described as “anthropogenic”, toward the ocean interior, is crucial today (Goyet and Touratier, 2009; Touratier et al., 2012).

Typical values of the Redfield ratios are those given by Redfield et al. (1963): the stoichiometric coefficients ψ_{O_2} , $\psi_{\text{NO}_3^-}$, and $\psi_{\text{PO}_4^{3-}}$ of Eq. (1) are equal to 138, 16 and 1 respectively, and lead to $R_{OP} = 138$, $R_{NP} = 16$ and $R_{ON} = 9$ (all numerical values are
20 rounded to the unit).

Since then, numerous studies have been conducted on the subject (see Sect. 3). They all confirm the Redfield's concept, but their results may give different values: depending on the studies, from 7 to 11 for R_{ON} , from 95 to 190 for R_{OP} , and from 12 to 26 for R_{NP} . Moreover, while Redfield established constant values at any point of the world ocean (the oceans are in open communication with each other, and constitute
25 the world ocean), the majority of them indicate that the Redfield ratios are variable

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according to ocean basin and to depth. This variability is further linked to the role of anthropogenic carbon, which does not penetrate in the same way everywhere in the ocean.

Here, we present a new method for determining the Redfield ratios. Like most other existing methods, it is based upon the inclusion of ocean circulation in addition to the composition of seawater. Its main interest is to be theoretically applicable everywhere (subject to the availability of sufficient independent data) while the other methods are in essence limited to particular zones.

2 Seawater composition

2.1 Hydrology

The two main characteristics of a seawater sample, in addition of its geographical position and its pressure (which is directly related to the depth at which it was taken), are its temperature and salinity. Seawater contains dissolved salts, in the form of ions (the main ones being the following six: Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-}). Salinity measures the amount of ions present in a kilogram of seawater.

Salinity of a seawater sample is determined by measuring its electrical conductivity compared to that of a solution of known salinity. Thus, since salinity is a ratio of conductivity, salinity is dimensionless.

2.2 Water masses

Under an appearance of stability, the ocean is in perpetual motion. Ocean circulation is mainly due to the exchanges of heat and gases with the atmosphere, and to the rotation of the Earth.

A “water mass” is a volume of water whose elements have the same history, i.e. have been formed in the same way in the same place (Tomczak, 1999). A water mass

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acquires its characteristics of temperature and salinity at surface, as a result of exchanges with the atmosphere, in well-defined water mass formation sites. Then, the water becomes heavier, it plunges and moves along surfaces of equal density.

As soon as the water mass has left the surface, its temperature and salinity can no longer change because there is no more exchange with the atmosphere: thus, they are called “conservative tracers”. They represent the signature of the water mass.

Along its journey, a water mass meets other water masses, with which it mixes. Thus, the features of the “conservative tracers” (temperature and salinity) in seawater vary from one ocean (geographical or depth) area to another due to the mixing of water masses.

Consider an area of the ocean where N water masses are present. In this area, any seawater sample results from the mixing of these water masses, in the proportions k_1, k_2, \dots, k_N called mixing coefficients. These coefficients satisfy:

$$\forall i \in \{1, 2, \dots, N\}, 0 \leq k_i \leq 1 \quad (5)$$

and:

$$\sum_{i=1}^N k_i = 1. \quad (6)$$

Any conservative characteristic C of a given sample verifies:

$$C = \sum_{i=1}^N k_i C_i \quad (7)$$

where C_i is the characteristic of the water mass i . The value of C depends only upon the mixing of the water masses at the considered location.

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2.3 Conservative tracers

There are other conservative tracers than temperature and salinity. Some are natural (like some radioactive elements due to cosmic rays), and some are artificial (such as CFCs, chlorofluorocarbons, which were manufactured and introduced into the atmosphere by Man).

Since their concentrations vary according to biological activity (as mentioned in Sect. 1), oxygen, nitrate and phosphate are not considered as conservative tracers. Their concentrations can be decomposed as the sum of a term reflecting the conservative mixing of water masses in the current sample, and a second term reflecting local biochemical processes:

$$[\text{O}_2] = \sum_{i=1}^N k_i [\text{O}_2]_i - \Delta \text{O}_2 \quad (8)$$

$$[\text{NO}_3^-] = \sum_{i=1}^N k_i [\text{NO}_3^-]_i + \Delta \text{NO}_3^- \quad (9)$$

$$[\text{PO}_4^{3-}] = \sum_{i=1}^N k_i [\text{PO}_4^{3-}]_i + \Delta \text{PO}_4^{3-}. \quad (10)$$

$[\text{O}_2]$, $[\text{NO}_3^-]$ and $[\text{PO}_4^{3-}]$ are the sample concentrations (in $\mu\text{mol kg}^{-1}$) of oxygen, nitrate, and phosphate, respectively. $[\text{O}_2]_i$, $[\text{NO}_3^-]_i$ and $[\text{PO}_4^{3-}]_i$ are the concentrations of the water mass i . The minus sign in Eq. (8) reminds that the oxygen is consumed when nitrate and phosphate are produced.

The Redfield's principle of variations in constant proportions, allows the construction of the tracers NO and PO (Broecker, 1974):

$$\text{NO} = [\text{O}_2] + R_{\text{ON}} [\text{NO}_3^-] \quad (11)$$

$$\text{PO} = [\text{O}_2] + R_{\text{OP}} [\text{PO}_4^{3-}] . \quad (12)$$

- 5 NO and PO are called “composite tracers” (each consisting of two non-conservative characteristics), and they are themselves conservative. Indeed, we get, by combining Eqs. (8), (9) and (11):

$$\text{NO} = \sum_{i=1}^N k_i [\text{O}_2]_i - \Delta \text{O}_2 + R_{\text{ON}} \left(\sum_{i=1}^N k_i [\text{NO}_3^-]_i + \Delta \text{NO}_3^- \right) \quad (13)$$

$$= \sum_{i=1}^N k_i \left([\text{O}_2]_i + R_{\text{ON}} [\text{NO}_3^-]_i \right) - \Delta \text{O}_2 + R_{\text{ON}} \Delta \text{NO}_3^- . \quad (14)$$

- 10 The concentrations variations respect: $\Delta \text{O}_2 = R_{\text{ON}} \Delta \text{NO}_3^-$ (cf. Eq. 2), so:

$$\text{NO} = \sum_{i=1}^N k_i \left([\text{O}_2]_i + R_{\text{ON}} [\text{NO}_3^-]_i \right) . \quad (15)$$

By defining the characteristic NO_i of the water mass:

$$\text{NO}_i = [\text{O}_2]_i + R_{\text{ON}} [\text{NO}_3^-]_i . \quad (16)$$

one finds again an equation (see Eq. 7) of a conservative tracer:

$$15 \quad \text{NO} = \sum_{i=1}^N k_i \text{NO}_i . \quad (17)$$

Thus, NO (and similarly PO) depends only upon the mixing of water masses at the considered point.

3 Theory

In order to determine the values of the Redfield ratios, existing methods generally seek to determine the non-conservative fractions ΔO_2 , ΔNO_3^- and ΔPO_4^{3-} of Eqs. (8)–(10). These fractions are proportional, and the proportionality coefficients directly produce the Redfield ratios.

A first category of methods (Alvarez-Borrego et al., 1975; Castro et al., 1998; Hupe and Karstensen, 2000; Schneider et al., 2005) begin to determine, for a given area, the various water masses in presence and their characteristics: $[\text{O}_2]_i$, $[\text{NO}_3^-]_i$ and $[\text{PO}_4^{3-}]_i$. Then, for each sample, the mixing coefficients k_i must be calculated. They allow to de-

termine the conservative parts of the oxygen and nutrient concentrations: $\sum_{i=1}^N k_i [\text{O}_2]_i$,

$\sum_{i=1}^N k_i [\text{NO}_3^-]_i$ and $\sum_{i=1}^N k_i [\text{PO}_4^{3-}]_i$. To access to the non-conservative fractions, then just subtract these conservative parts to the corresponding measured concentrations $[\text{O}_2]$, $[\text{NO}_3^-]$ and $[\text{PO}_4^{3-}]$. The disadvantage of these methods lies in the errors in the estimation of the mixing coefficients. First, the characteristics of a water mass can never be determined exactly. Then, the mixing coefficients can be calculated only sample by sample, without the possibility to reduce errors by using a global calculation on all samples.

A second category of methods does not explicitly determine the mixing coefficients. From assumptions upon the various water masses in the vicinity, they build relationships (other than simple proportionality) between concentrations $[\text{O}_2]$, $[\text{NO}_3^-]$ and $[\text{PO}_4^{3-}]$. The identification of the parameters of these relationships leads to the Redfield ratios. But these methods are only applicable either to specific areas (Takahashi et al., 1985; Minster and Boulahdid, 1987; Shaffer et al., 1999; Li and Peng, 2002; Schroeder et al., 2010), or to areas where at the most two water masses mix (Anderson and Sarmiento, 1994; Placenti et al., 2013).

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The advantage of the method presented here, is that first, it does not require the identification of characteristics of each water mass, nor any knowledge about the mixing coefficients. Thus, it eliminates a primary source of errors. Secondly, if there are enough data available, it can be applied everywhere, whatever the area, and its application is always done in the same way.

3.1 Assumptions and notations

Let us consider P samples of seawater, spread in an area of the world ocean where N water masses (known also as “sources”) are present. We suppose that for each sample, we have measurements of M conservative tracers with $P \geq M$.

We can build the matrix \mathbf{D} (P rows \times M columns) of data:

$$\mathbf{D} = \begin{pmatrix} \vdots & \vdots & & \vdots \\ d_{l,1} & d_{l,2} & \cdots & d_{l,M} \\ \vdots & \vdots & & \vdots \end{pmatrix}. \quad (18)$$

For each measurement point l , $1 \leq l \leq P$, the corresponding values $d_{l,1}, d_{l,2}, \dots, d_{l,M}$ of the M conservative tracers are in row l . For example, the first column of the matrix \mathbf{D} can be composed of temperature data, and the second column of salinity data.

Note $\mathbf{1}_P$ the vector of P rows and one column, whose all elements are equal to 1:

$$\mathbf{1}_P = \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix}. \quad (19)$$

The starting point of our method is based on the following question:

Is there a vector \mathbf{a} of M real coordinates, $\mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_M \end{pmatrix}$, such that

$$\mathbf{D}\mathbf{a} = \mathbf{1}_P? \quad (20)$$

Let \mathbf{K} be the matrix (P rows \times N columns) of mixing coefficients:

$$\mathbf{K} = \begin{pmatrix} \vdots & \vdots \\ k_{I,1} & k_{I,2} & \cdots & k_{I,N} \\ \vdots & \vdots \end{pmatrix}. \quad (21)$$

5 For each sample I , $1 \leq I \leq P$, the corresponding mixing coefficients $k_{I,1}, k_{I,2}, \dots, k_{I,N}$ are in row I . Their sum being equal to 1 (cf. Eq. 6), we have:

$$\mathbf{K}\mathbf{1}_N = \mathbf{1}_P \quad (22)$$

where $\mathbf{1}_N$ is the vector of N rows \times 1 column, whose all elements equal 1.

Let \mathbf{W} be the matrix (N rows \times M columns) of the characteristics of sources:

$$10 \quad \mathbf{W} = \begin{pmatrix} \vdots & \vdots \\ w_{I,1} & w_{I,2} & \cdots & w_{I,M} \\ \vdots & \vdots \end{pmatrix}. \quad (23)$$

For each water mass I , $1 \leq I \leq N$, the corresponding conservative tracers $w_{I,1}, w_{I,2}, \dots, w_{I,M}$ are in row I . As all considered tracers are conservative, Eq. (7) becomes, in matrix form:

$$\mathbf{D} = \mathbf{K}\mathbf{W}. \quad (24)$$

15 It is necessary to define \mathbf{K} and \mathbf{W} to demonstrate that the vector \mathbf{a} exists, but it is not necessary to know their values to apply our method (and this is the main advantage of this method).

3.2 Existence of a linear relation between conservative tracers

Let us concentrate here to solve Eq. (20). In other words, do M conservative tracers make an hyperplane in R^M ?

Furthermore, suppose that the N sources are independent (none is the result of a mixing of the others). In practice, it is mainly the knowledge of the hydrology of the ocean area which ensures correct identification of the independent water masses. Thus, the rank of the matrix \mathbf{D} is equal to the minimum of N and M . Three cases are possible (referring to the results on the resolution of a linear system):

– *Case 1: $N > M$* (more water masses than conservative tracers)

Then, the rank of matrix \mathbf{D} is equal to M . So we know that the only possible solution of the equation $\mathbf{D}\mathbf{a} = \mathbf{1}_P$ is the solution in the least-squares sense:

$$\mathbf{a}_{mc} = (\mathbf{D}'\mathbf{D})^{-1}\mathbf{D}'\mathbf{1}_P \quad (25)$$

where the apostrophe operator (\prime) stands for the transpose matrix.

The vector \mathbf{a}_{mc} minimizes the norm of the residuals of the equation $\mathbf{D}\mathbf{a} = \mathbf{1}_P$, but there is no guarantee that this minimum is equal to zero, or in other words that \mathbf{a}_{mc} is a exact solution of the equation. Moreover, in general, it is not! So in this case, there is a priori no hyperplane of the tracers.

– *Case 2: $N < M$* (less water masses than conservative tracers)

Then, the rank of \mathbf{D} is equal to N . So we know nothing about $\mathbf{D}\mathbf{a} = \mathbf{1}_P$.

Consider the same equation, not anymore on data but on sources:

$$\mathbf{W}\mathbf{a} = \mathbf{1}_N. \quad (26)$$

The rank of matrix \mathbf{W} is equal to N . So Eq. (26) has at least one (exact) solution, the vector

$$\mathbf{a}_s = \mathbf{W}'(\mathbf{W}\mathbf{W}')^{-1}\mathbf{1}_N. \quad (27)$$

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(There is no guarantee that this solution is unique, but this is not a problem for our final objective.)

This solution satisfies:

$$\mathbf{W} \mathbf{a}_s = \mathbf{1}_N \quad (28)$$

hence, by multiplying on the left by \mathbf{K} :

$$\mathbf{K} \mathbf{W} \mathbf{a}_s = \mathbf{K} \mathbf{1}_N \quad (29)$$

or, by using Eq. (22):

$$\mathbf{K} \mathbf{W} \mathbf{a}_s = \mathbf{1}_P \quad (30)$$

and finally, with Eq. (24):

$$\mathbf{D} \mathbf{a}_s = \mathbf{1}_P. \quad (31)$$

In other words, \mathbf{a}_s is also a solution of the first equation on data (Eq. 20). So in this case, the tracers form at least one hyperplane.

- *Case 3: $N = M$* (as many water masses as conservative tracers) This case falls in both the second case (rank of \mathbf{D} equal to N) and in the first case (rank of \mathbf{D} equal to M). The equation $\mathbf{D} \mathbf{a} = \mathbf{1}_P$ therefore has a unique solution, which is:

$$\mathbf{a}_s = (\mathbf{D}' \mathbf{D})^{-1} \mathbf{D}' \mathbf{1}_P. \quad (32)$$

Or equivalently, since here \mathbf{W} is invertible:

$$\mathbf{a}_s = \mathbf{W}^{-1} \mathbf{1}_N. \quad (33)$$

In conclusion, if $N \leq M$ (as many or more conservative tracers than water masses), we know that there exists a linear relation between the M conservative tracers.

We will see in Sect. 4 how to find the coefficients of this relation, using an algorithm of total least-squares (Markovsky and Van Huffel, 2007). For now, we have demonstrated the existence of a relation, but we have no means of getting it. If $N < M$, the vector $\mathbf{a}_s = \mathbf{W}'(\mathbf{W}\mathbf{W}')^{-1}\mathbf{1}_N$ (cf. Eq. 27) is incalculable since the matrix \mathbf{W} is unknown. If $N = M$, the Eq. (33) fails to provide the solution (since \mathbf{W} is still unknown) and the Eq. (32) cannot be applied directly. Indeed, the computation of the pseudoinverse (matrix $(\mathbf{D}'\mathbf{D})^{-1}\mathbf{D}'$) of the matrix \mathbf{D} is so sensitive to the unavoidable noise (of the measured data) that it often leads to unusable results.

3.3 Principle of the determination of the Redfield ratios

Let us now assuming $N \leq M$. This restricts the use of our method to areas where sufficient measurement data are available compared to the water masses involved.

How the existence of a linear relation between the conservative tracers permits to determine the Redfield ratios? Just take, among the tracers, the composite tracers NO or PO. We now know that there exists a linear relation between these composite tracers and the other considered tracers. The estimate of this linear relationship, which has the minimum error, will correspond to the correct value of the coefficients R_{ON} or R_{OP} (in the calculation of NO or PO).

For example, consider an area where we have at our disposal data of temperature T , salinity S , oxygen $[\text{O}_2]$ and nitrate $[\text{NO}_3^-]$, and where there are at maximum three water masses. The tracer NO is given by Eq. (11), in which the value of R_{ON} is the unknown to be determined. From now on, we know that there exist a_1, a_2, a_3 in R such that, when the value taken for R_{ON} is the correct one, the data of every sample in the area satisfy the equation:

$$a_1 T + a_2 S + a_3 \text{NO} = 1. \quad (34)$$

The correct value of R_{ON} is that minimizing the error of reconstruction of Eq. (34).

Note that we can write Eq. (34) in the form:

$$a_1 T + a_2 S + a_3 [\text{O}_2] + a_3 R_{\text{ON}} [\text{NO}_3^-] = 1. \quad (35)$$

Hence, if we set

$$a_4 = a_3 R_{\text{ON}} \quad (36)$$

5 we have:

$$a_1 T + a_2 S + a_3 [\text{O}_2] + a_4 [\text{NO}_3^-] = 1. \quad (37)$$

Thus, we can also determine a_1 , a_2 , a_3 , a_4 and then apply:

$$R_{\text{ON}} = \frac{a_4}{a_3}. \quad (38)$$

4 Data and calculation

10 4.1 Conservative tracers

The data that we have used are those of GLODAP database (Key et al., 2004), which covers the global ocean by combining a wide set of oceanographic measurements. Measurements of different expeditions since 1990, through all oceans, were synthesized and calibrated to provide a global database. In GLODAP, there are measurements of temperature, salinity, oxygen, nitrate, and phosphate. Oxygen and nitrate lead to the conservative tracer NO while oxygen and phosphate lead to PO. Temperature and salinity are used directly as conservative tracers.

15 Strictly speaking, because of the slight compressibility of sea water, which causes a warming due to pressure, the temperature “in situ” (archived in GLODAP) is not exactly a conservative parameter because it varies with pressure. The laws of thermodynamics permit to calculate the temperature corrected for the pressure effect (see the

official site <http://www.teos-10.org/> about the Thermodynamic Equation Of Seawater). It is this conservative temperature that we calculated and used. Similarly, we calculated the “preformed” salinity which is strictly conservative. It is also calculated from the measured salinity, according to the same laws of thermodynamics. It is the one we used here.

Moreover, the measurements available in GLODAP allow us to build another composite tracer: TrOCA^0 . It is made from temperature and total alkalinity (total alkalinity measures the excess of basic species over acid species in seawater). Its precise definition and its properties are described in Touratier and Goyet (2004) and Touratier et al. (2007). Here, its interest is to be conservative.

So we have five conservative tracers: (conservative) temperature T , (preformed) salinity S , NO , PO and TrOCA^0 . We recall that we have demonstrated in the preceding paragraphs, the existence of a linear relation between any set of M conservative tracers, in any area comprising at maximum M water masses. In addition, the fact of taking NO or PO among the M tracers enables to determine the Redfield ratios: the correct values of R_{ON} or R_{OP} are those minimizing the error of reconstruction of the linear relation between tracers.

4.2 Measurement noise

Let us continue the example already given in Sect. 3.3 of computing R_{ON} in an ocean area with a maximum of three water masses (in an area with four water masses, we would use TrOCA^0 in addition to temperature and salinity). In order to determine R_{ON} , we have two possibilities. The first one, is to directly determine the four coefficients of the linear relation (Eq. 37) and then to calculate R_{ON} using the Eq. (38). The second one, is a minimization loop on the values of R_{ON} : we successively assume different values for R_{ON} ; for each assumed value of R_{ON} , we compute the tracer NO (Eq. 11) and we determine the three coefficients of the Eq. (34) as well as the norm of the residuals of this Eq. (34). Finally, we choose the correct value of R_{ON} as the one corresponding to the smallest norm of residuals.

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If the data were free from noise, the above two options would lead to the same result. But of course, the available data are noisy! They are supposed to be affected by additive Gaussian noise with zero mean and standard deviation depending on the data type: 0.001 °C for temperature, 0.0001 for salinity, 0.02 μmol kg⁻¹ for nitrate, 0.005 μmol kg⁻¹ for phosphate, 2 μmol kg⁻¹ for oxygen.

The presence of noise makes crucial the choice of the calculation method. The second of the above two possibilities is not satisfactory because it too often leads to a divergence of the minimization algorithm. Thus, we wrote our calculation program by choosing the first option, i.e. by decomposing the tracer NO to arrive at Eq. (37).

Similarly, in order to calculate R_{OP} , we must determine the four coefficients b_1, b_2, b_3, b_4 of the equation:

$$b_1 T + b_2 S + b_3 [O_2] + b_4 [PO_4^{3-}] = 1 \quad (39)$$

then calculate:

$$R_{OP} = \frac{b_4}{b_3}. \quad (40)$$

The determination of R_{ON} and of R_{OP} are thus made independently. In theory, one can imagine a simultaneous calculation of R_{ON} and R_{OP} . Just construct a double minimization loop through the values of both R_{ON} and R_{OP} , in order to minimize the residuals of an equation involving both the tracer NO and the tracer PO:

$$\alpha_1 T + \alpha_2 S + \alpha_3 NO + \alpha_4 PO = 1. \quad (41)$$

In practice, this double loop, as the previously envisaged simple loop, often diverges (here again, because of the presence of noise in the data). We therefore did not keep it as a valid algorithm.

Note that, since we cannot use both NO and PO tracers simultaneously, we are reduced to up to four conservative tracers: for the estimation of R_{ON} , temperature,

salinity, TrOCA^0 and NO_3^- ; for the estimation of R_{OP} , temperature, salinity, TrOCA^0 and PO. Consequently, we will be limited to study ocean areas with a maximum of four water masses. For most ocean areas, as shown below (for example for the Atlantic Ocean), this is just fine since we can often split a large area in smaller areas. Yet, for an ocean area with more than four water masses, the calculation algorithm would remain the same but it would require additional conservative tracers (CFCs, for example).

4.3 Estimation of the Redfield ratios

Returning to Eq. (37), it is now necessary to estimate its coefficients, in order to then determine R_{ON} (with Eq. 38). In order to calculate R_{OP} , the approach is identical, from the Eq. (39) and then Eq. (40).

It is a least-squares problem, but in which the data are noisy and the noises have different standard deviations. Furthermore, in Eq. (37), the second term of equality is not zero but equal to 1. The robust estimator is therefore the Generalized Total Least-Squares estimator (Markovsky and Van Huffel, 2007). In order to compute this estimator, we should write the equation in the form:

$$a_1 T + a_2 S + a_3 [\text{O}_2] + a_4 [\text{NO}_3^-] - 1 = 0 \quad (42)$$

or:

$$a_1 T + a_2 S + a_4 [\text{NO}_3^-] - 1 = -a_3 [\text{O}_2] \quad (43)$$

or finally:

$$x_1 T + x_2 S + x_3 [\text{NO}_3^-] + x_4 = [\text{O}_2] \quad (44)$$

or, in matrix form:

$$\mathbf{A} \mathbf{x} = \mathbf{b} . \quad (45)$$

For every measurement point l , note T_l , S_l , $[\text{NO}_3^-]_l$ and $[\text{O}_2]_l$ the corresponding data values. The first column of the matrix \mathbf{A} contains temperature data, the second column those of salinity, the third column those of nitrate, and the fourth column consists of constant values equal to 1:

$$\mathbf{A} = \begin{pmatrix} \vdots & \vdots & \vdots & 1 \\ T_l & S_l & [\text{NO}_3^-]_l & 1 \\ \vdots & \vdots & \vdots & 1 \end{pmatrix}. \quad (46)$$

The vector \mathbf{b} contains the measurements of oxygen:

$$\mathbf{b} = \begin{pmatrix} \vdots \\ [\text{O}_2]_l \\ \vdots \end{pmatrix}. \quad (47)$$

The vector

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix} \quad (48)$$

is that of the parameters to be estimated.

Equation (38), which allowed us to determine the value of R_{ON} , becomes:

$$R_{\text{ON}} = -x_3. \quad (49)$$

The non-zero second term of the initial Eq. (37) therefore results in a constant column in the matrix \mathbf{A} (i.e. a column without noise). To get an estimate as robust as possible, the vector \mathbf{b} must contain the noisiest data (oxygen).

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Furthermore, our problem is an “ill-posed” inverse problem: the matrix containing all the measurement data is ill-conditioned, due to both the additive noise and the significant differences in the orders of magnitude among the tracers. This bad conditioning prohibits any direct pseudoinverse solution. On the contrary, in order to “regularize” the problem, the estimation algorithm suggests truncation, if necessary, of the lowest eigenvalues of this matrix.

Provided that a solution exists, the method of Generalized Total Least-Squares gives an analytical formulation of the result, which is much more reliable than a result that would have been found by a local optimization. Hence it was very important to first demonstrate that a solution exists.

Finally, let us note that among the measurement points, there are always a few of them that are aberrant (at these points, the measurements were, for various reasons, totally biased and flawed). To overcome this issue, we iteratively calculate the estimate: on every iteration, we remove the data points that are three times above the standard deviation of the residuals of the estimation.

We wrote the estimation algorithm using MATLAB.

5 Results and discussion

5.1 Study areas

5.1.1 The Atlantic Ocean

We chose to test this method in the Atlantic Ocean because it is a key element in the large-scale circulation of the global ocean. That’s basically it which connects the two polar oceans (the Antarctic and Arctic Oceans). The exchanges between the Arctic Ocean and the Pacific Ocean are limited to the Bering Strait, while on the contrary, the Arctic Ocean is open onto the Atlantic Ocean by the Nordic Seas (the Norwegian Sea,

the Greenland Sea and the Iceland Sea). The Atlantic Ocean is thus a privileged place of transformation of surface waters into deepwater.

North of the Atlantic Ocean, under the effects of cooling and evaporation, surface waters of the Nordic Seas become denser and plunge, creating the North Atlantic Deep Water, or NADW. The NADW flows at deep southward, following the American continent, and joins the deep circumpolar circulation that transports the cold and dense waters formed along the Antarctic continent. These waters mix to form the AntArctic Bottom Water, or AABW, and feed the Indian and Pacific Oceans, where they slowly rise to the surface while warming up. Then, these warmer surface waters join the North Atlantic Ocean, and the process starts again (the time required for a water particle to perform this cycle is about a thousand years).

Since the method presented here needs not to have more water masses than conservative tracers, it requires to “cut” the Atlantic Ocean in several zones.

In an area where there are N sources and where M tracers are available, the M values of these tracers, for each measurement point, are the coordinates of the faces of a convex polyhedron of dimension M , with N vertices. The projection of this polyhedron on a plane (formed for example by the temperature and salinity tracers, which gives the “diagram T–S”), is a polygon having X vertices, with $X \leq N$, each vertex of the polygon corresponding to one of the sources. Such projection is often used to determine the number and position of the sources involved, by identifying the vertices of the polygon. But the determination of the vertices of the polygon has variable accuracy, depending upon the respective positions of the available measurement points. Moreover, as there is no guarantee that X equals N , $(N - X)$ sources are absolutely inaccessible.

Consequently, a zoning based solely on the measurement points would be absurd. Here, we identified 16 areas in the Atlantic Ocean, based not only upon the available data (via the T–S diagram), but also mainly on the current knowledge of the water masses and their movements (Fieux, 2010).

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5.1.2 Latitudes

The longitudinal limits of the Atlantic Ocean are the natural continental limits. The Atlantic Ocean is limited to the west by the American coasts and to the east by the European and African coasts. The hydrological characteristics of the Atlantic Ocean allow to divide it into four latitudinal zones, as shown in Fig. 1 and defined as follows:

- The North Atlantic Ocean, at latitudes ranging from 60° N to 20° N (in red in Fig. 1). Beyond 60° N, there is the Arctic Ocean.
- The northern Equatorial Atlantic Ocean, at latitudes ranging from 20° N to 5° N (in yellow in Fig. 1).
- The southern Equatorial Atlantic Ocean, at latitudes ranging from 5° N to 20° S (in pink in Fig. 1). This part includes the equator and its specific oceanic movements.
- The South Atlantic Ocean, at latitudes ranging from 20° S to 45° S (in green in Fig. 1). The limit of 45° S is determined between the Subtropical Front (a “Front” is a place of convergence of different water masses) and the Polar Front. South of the Polar Front, there is the Antarctic Ocean, where ocean circulation is very different.

5.1.3 Depths

At these latitudinal zones, one should add depth ranges. First, recall that we must consider only the data from below the mixed layer (cf. Sect. 1). For this, we used the database NDP-076 (Goyet et al., 2000), which gives the maximum depth of the mixed layer, for each month of the year, at any point of the world ocean (on a grid of 1° longitude by 1° latitude). Then, the characteristics of ocean circulation can distinguish three layers:

- the surface ocean, at depths ranging from 50 m down to 500 m;

- the intermediate layer, at depths between 500 and 1750 m;
- the deep ocean, at depths deeper than 1750 m.

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is also subject to the influence of other sources of less importance, and of more or less distant origin. Neglecting these other sources when estimating the Redfield ratios is possible only if the choice of the measurement points considered for an estimate, and therefore the definition of study areas, remain based on previous knowledge of ocean movements.

Two deep water masses are present at all latitudes of the Atlantic Ocean: the AntArctic Bottom Water (AABW) and the North Atlantic Deep Water (NADW). The AABW is the deepest water mass: it lies over the entire bottom of the Atlantic Ocean, below 4000 m. The NADW has its origin in the Nordic Seas and flows southward along the American continent. It is present in all deep layers except in the northeast. It can be divided into three sources: the upper NADW at depths between 1200 and 1900 m, the central NADW between 1900 and 3500 m, the lower NADW between 3500 and 3900 m.

Another water mass, less deep, can also be found at almost at all latitudes: the AntArctic Intermediate Water (AAIW). It originates from the Antarctic Ocean, and flows northward to a maximum latitude of about 20° N. Its presence is less strong in the east than in the west. With an average depth of 1000 m, it influences the intermediate layer (between 500 and 1750 m) but also the deep layer (beyond 1750 m).

The Central or Subtropical waters are water masses with a more limited geographical spread, and a relatively shallow depth range (average depth between 500 and 700 m). They are formed in convergence zones, where waters tend to dive due to wind forcing. The North Atlantic SubTropical Water (NASTW) and the North Atlantic Central Water (NACW) are created north of the equator while the South Atlantic SubTropical Water (SASTW) and the South Atlantic Central Water (SACW) are created south of the equator. Note that the NACW is subjected to intense winter cooling, causing a convection (vertical mixing) significantly deeper than in southern Atlantic Ocean, and hence it can mix with water from the bottom layer.

In addition to these main water masses, there are water masses of local influence. Among them, two are deep sources: in the northwest, there is the Denmark Strait Overflow Water (DSOW), at depths between 3000 and 3500 m; in the northeast, there

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is the Iceland–Scotland Overflow Water (ISOW), at depths between 2000 and 2500 m. An intermediate water mass, the Mediterranean Water (MW), enters the Atlantic Ocean through the Strait of Gibraltar, in the northeast, and stabilizes at an average depth of 1000 m. In the surface layer, local sources have characteristics directly related to the various exchanges of heat and water with the atmosphere, and they are therefore relatively variable. These sources have no specific name. We have found a different local source in each surface zone.

5.3 Redfield ratios

Table 2 shows the results obtained for each zone. We estimated R_{ON} and R_{OP} independently, using NO for the calculation of R_{ON} and using PO for the calculation of R_{OP} (cf. Sect. 4.3).

In order to determine the accuracy of these results, a first measurement, statistical, is given by the coefficient of determination r^2 . This coefficient measures the validity of the result vector x found for Eq. (45) (it measures how successful the result x is in explaining the variation of the data). r^2 can take on any value between 0 and 1, with a value closer to 1 indicating a greater goodness of fit. For the 16 areas considered here, whether it is calculation of R_{ON} or calculation of R_{OP} , r^2 always remains above 0.84, and equals on average 0.94.

A second measurement, probabilistic, is given by the standard deviation of the estimated R_{ON} or R_{OP} ratios. By analogy with the formula for the standard deviation of the Least-Squares estimator (Markovsky and Van Huffel, 2007), we determined a standard deviation equal at maximum to 0.125 for R_{ON} and to 2.73 for R_{OP} (or approximately 2 % of the result). These values allowed to determine the 99 % confidence interval of the results: ± 0.3 for R_{ON} values and ± 6 for R_{OP} values.

Table 2 also indicates values of the R_{NP} ratio. This R_{NP} ratio is not estimated directly from the data, but it is deducted from the results obtained for the first two ratios (according to Eq. 4: $R_{\text{NP}} = R_{\text{OP}}/R_{\text{ON}}$).

Overall, the first striking result is that the values obtained for the ratios, are remarkably near-constant! They vary relatively little from one zone to another, which is in good agreement with the existence of the Redfield's concept.

Furthermore, our results are very close to those first given by Redfield himself in 1963 (Redfield et al., 1963). Nevertheless, the values here are in general, slightly lower than those estimated by Redfield ($R_{ON} = 9$ and $R_{OP} = 138$). However, in view of our method (selection of study areas according to the hydrological characteristics and then use of an identical estimator whatever the area), the variations in these values from one area to another are certainly more significant than the values themselves.

We detect significant variations both in latitude and in depth. From north to south (from 60° N to 45° S), regardless of depth, R_{ON} decreases and then increases, R_{OP} increases and then decreases, and therefore R_{NP} ($R_{NP} = \frac{R_{OP}}{R_{ON}}$) increases and then decreases. When the depth increases, regardless of latitude, both R_{ON} and R_{OP} increase and then decrease, thus R_{NP} decreases and then increases (since the numerator R_{OP} varies less than the denominator R_{ON}).

In the literature, several studies report various values for the Redfield ratios. Often, these values also differ from those of Redfield himself, and this to a greater or lower extent (depending on the study, R_{ON} can range from 7 to 11, R_{OP} can range from 95 to 190, R_{NP} can range from 12 to 26). In general, they also vary geographically, depending both upon the area and upon the depth.

But the results (as well as the zones that are considered) are different depending on the methods used, and their associated explanations are more or less related to local phenomena. Thus, it is very difficult to compare results (Schneider et al., 2005). Some can be interpreted as similar to ours, others not.

For example, Anderson and Sarmiento (1994) calculated R_{OP} and R_{NP} in the south Atlantic (20° N to 50° S), Indian (20° N to 30° S) and south central Pacific (between 10° N and 30° S) basins, between 400 and 4000 m depth. They found that the R_{OP} ratio is constant with depth and basin, at a value of 170 ± 10 , whereas R_{NP} is constant with basin but exhibits a mid-depth minimum: in the 1000–3000 m zone, $R_{NP} \cong 12 \pm 2$,

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above and below $R_{NP} \cong 16 \pm 1$ (consequently, R_{ON} varies from approximately 11 to 14 at mid-depth).

Shaffer et al. (1999) analyzed data chosen in the same three ocean sectors (low- and mid-latitude Pacific, Indian and south Atlantic oceans) and obtained once again ratios constant with basin. But they estimated that R_{OP} increases from about 140 at 750 m depth to about 170 at 1500 m and remains so deeper down. R_{NP} was found to decrease from about 15 at 750 m to about 12 at 1500–2000 m, similar to results from Anderson and Sarmiento.

On a smaller scale, Hupe and Karstensen (2000) estimated R_{OP} and R_{NP} within the Arabian Sea between 550 and 4500 m. Both ratios were found to increase continuously with depth. In the 550–1200 m zone, $R_{OP} \cong 139 \pm 7$ and $R_{NP} \cong 14.4 \pm 0.2$. Between 1200 and 2000 m, $R_{OP} \cong 152 \pm 5$ and $R_{NP} \cong 14.9 \pm 0.2$. Deeper than 2000 m, $R_{OP} \cong 158 \pm 5$ and $R_{NP} \cong 15.3 \pm 0.2$. No mid-depth minimum was observed for R_{NP} .

Li and Peng (2002) did not reveal any variation with depth but showed, for the Atlantic Ocean divided into two zones: 45° N to 5° N, and 5° N to 50° S, a decrease of each ratio R_{ON} , R_{OP} , R_{NP} from north to south. In the northern zone, $R_{ON} \cong 8.5 \pm 0.8$, $R_{OP} \cong 137 \pm 7$ and $R_{NP} \cong 16.1 \pm 1.0$. In the southern zone, $R_{ON} \cong 8.4 \pm 0.3$, $R_{OP} \cong 128 \pm 5$ and $R_{NP} \cong 15.2 \pm 0.7$.

Today, the only agreed-upon conclusions are both the confirmation of the Redfield's concept (which has also been extended to other ecosystems than in the ocean), and the variability of these ratios depending upon the ocean area.

This variability seems natural: biogeochemical processes do not occur in the same way everywhere, even if they are somewhat homogenized by large-scale ocean circulation. In the upper layer of the ocean in contact with the atmosphere, the carbon and nutrients concentrations are far from being homogenized. At depth, nutrients are generally remineralized at about 1000 m. The water masses movements and mixing, which tend to homogenize the nutrients and carbon concentrations, vary geographically.

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Moreover, since the industrial era, the anthropogenic parts of carbon dioxide and also of nitrate and phosphate, are rising sharply. It is likely that this anthropogenic phenomenon accentuates the spatial variability of the Redfield ratios, and thus may add a temporal variability to these ratios.

6 Conclusions

Redfield ratios are prime indicators of the chemical composition of the ocean, which is governed by biological, chemical and physical processes. In the upper layer of the ocean, photosynthesis transforms carbon and nutrients into organic matter. This organic matter then remineralizes at depth, allowing the different elements to be entrained in a huge (large-scale) cycle through the convection movements and ocean circulation. In the context of climate change, these biogeochemical processes are very important because they determine how fast the ocean can absorb carbon dioxide from the atmosphere.

From the notion of water masses circulation and conservative tracers, we built the Generalized Total Least-Squares estimator of the Redfield ratios R_{ON} and R_{OP} . We have tested it, over the Atlantic Ocean from 60° N down to 45° S. The results remain close to the nominal values of Redfield, with a variability consistent with some previous studies. The precise determination of the Redfield ratios is particularly important today in the context of global change, since they are used to calculate the concentrations of anthropogenic carbon that penetrates into the ocean. The variability of these ratios demonstrates the need for a detailed study of their values prior their use, and the limitations of any mean that could be done.

Therefore, the method presented here could be particularly useful for future studies. While it respects the hydrological specificities of each ocean area, it can simply be applied everywhere, in an analytical manner (so without the risks of local artifact or divergence that an optimization algorithm would have), always constructing the same estimator. This is obviously subject to available measurements.

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The estimation of R_{ON} is based on the use of the conservative tracer NO, and therefore always needs the data of oxygen and nitrate. Similarly, the estimation of R_{OP} is based on the use of the conservative tracer PO, and therefore always needs the data of oxygen and phosphate. The other measurement data can be variable, as long as they allow to build enough conservative tracers for the considered area.

For example here, to determine the Redfield ratios in the Atlantic Ocean, we used the “in situ” measurements: inevitably, oxygen, nitrate and phosphate (for NO and PO), then temperature, salinity and total alkalinity. From these “in situ” measurements, we built conservative tracers: conservative temperature, conservative salinity (so-called preformed), and tracer TrOCA^0 (it is the one that needs the measurements of total alkalinity). But the method would apply in the same way to different measurements and tracers.

The other advantage of this method, is that it also includes the anthropogenic part of the chemical elements involved (carbon, nitrate and phosphate). This is particularly important since today, the anthropogenic concentrations of carbon, nitrate and phosphate in the ocean are increasing.

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Table 1. Study areas and their water masses.

	50–500 m	500–1750 m	1750 m–bottom	
			West	East
60° N–20° N	a surface water NASTW NACW	NASTW NACW MW	NACW central NADW DSOW AABW	MW NACW ISOW AABW
20° N–5° N	a surface water NASTW SASTW NACW	NASTW SASTW AAIW upper NADW	AAIW upper NADW lower NADW AABW	upper NADW lower NADW AABW
5° N–20° S	a surface water SASTW SACW	SASTW AAIW upper NADW	AAIW upper NADW lower NADW AABW	AAIW upper NADW lower NADW AABW
20° S–45° S	a surface water SASTW AAIW	SASTW AAIW upper NADW	AAIW upper NADW lower NADW AABW	AAIW upper NADW lower NADW AABW

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Table 2. Redfield ratios, within each studied ocean area.

	50–500 m			500–1750 m			1750 m–bottom					
	R_{ON}	R_{OP}	R_{NP}	R_{ON}	R_{OP}	R_{NP}	West			East		
	R_{ON}	R_{OP}	R_{NP}	R_{ON}	R_{OP}	R_{NP}	R_{ON}	R_{OP}	R_{NP}	R_{ON}	R_{OP}	R_{NP}
60° N–20° N	7.3	127	17.4	8.8	131	14.9	8.1	122	15.1	8.1	124	15.3
20° N–5° N	7.2	127	17.6	8.7	132	15.2	7.6	123	16.2	7.7	125	16.2
5° N–20° S	7.1	130	18.3	8.7	133	15.3	7.2	126	17.5	7.4	126	17.0
20° S–45° S	7.7	123	16.0	9.1	132	14.5	8.2	125	15.2	8.2	126	15.4

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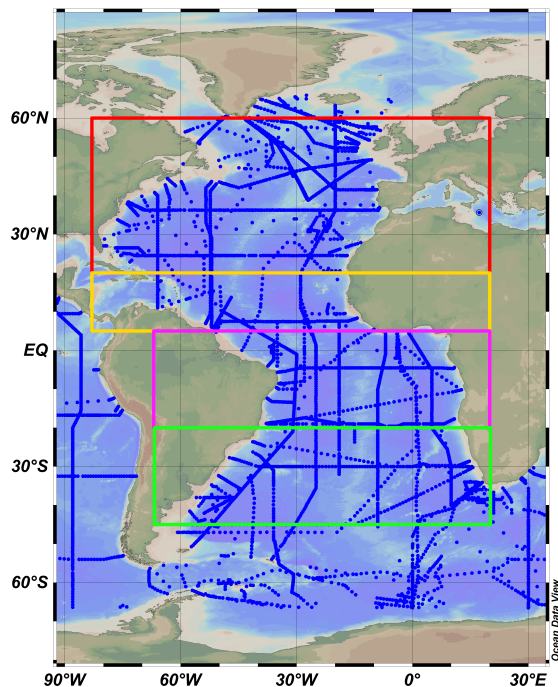


Figure 1. The Atlantic Ocean.