

A modelling approach to the Redfield ratio deviations in the ocean*

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SUMMARY: A study of the relationship among $-\Delta O_2$, ΔN and ΔC was developed when the production or mineralisation of particulate organic matter do not follow the Redfield ratios. A dinoflagellate red tide and a diatom spring bloom are shown as two cases where these Redfield deviations can be found. We propose a new useful tool for modelling water mass mixing and net community production budgets, which includes a chemical parameter (" NCO " = $O_2 + R_N \cdot NO_3(1 - R_{CS}/R_C) + R_{CS} \cdot CO_2$) of general application where " NCO " indicates the involved variables (Nitrate- CO_2 -Oxygen). R_N and R_C are the fixed Redfield ratios and R_{CS} is the relationship between oxygen consumed and CO_2 assimilated corresponding to storage substances. The R_{CS} value depends on the nature of the storage substances. Generally these substances are carbohydrates and the value of $R_{CS}=1$.

Key words: Redfield ratio, stoichiometry, " NO ", " CO ", " NCO ", organic matter

INTRODUCTION

Models of global nutrient budgets, net production and mixing of water masses in the ocean, have commonly assumed that synthesis and remineralization of particulate organic matter occurs according to the Redfield composition. However, that is an oversimplification because sometimes phytoplankton photosynthesis follows deviations to this rule (e.g. Cullen, 1985, Fraga *et al.*, 1992, Sambrotto *et al.*, 1993). For this reason, it is necessary to overcome this problem in order to achieve a better resolution in global production-regeneration and water mass models.

During photosynthesis and remineralization processes of particulate organic matter in the ocean, the ratios between oxygen and nutrient variations are almost constant. Redfield *et al.* (1963), starting from elementary analysis of plankton samples, established the ratios: $-\Delta O_2$: ΔC : ΔN : ΔP to be 138:106:16:1, where $-\Delta O_2$ was estimated from the oxidation of $106 CH_2O + 16 NH_4$. However, as Redfield had already pointed out, the ratios can vary when more reduced molecules, such as lipids, are considered. Lipids consume about 36% more oxygen than carbohydrates during their oxidation. Therefore, considering that the average of lipid and carbohydrate contents of the particulate organic matter are 24% and 17% respectively, the elementary composition must be $C_{106}H_{171}O_{42}N_{16}P$ (Anderson, 1995, Fraga *et al.*, 1998) and the $-\Delta O_2$: ΔC : ΔN : ΔP ratios should be 149:106:16:1.

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This elementary composition is found in coastal and open ocean waters at many times and locations, but on some occasions, the relatively high synthesis of storage material (carbohydrates and lipids), can alter the modified Redfield ratios (Fraga *et al.*, 1992, Banse, 1994, Richardson and Cullen, 1995, Moore and Villareal, 1996). Deviations to these ratios also occur when this organic matter, rich in storage compounds, is remineralized in a different water column level from that where it was produced, as happens during the sinking of particulate organic matter (Tanoue, 1985). High synthesis of storage compounds usually occurs at the end of phytoplankton spring blooms when the population can only synthesize storage substances because nutrient depletion precludes protein synthesis. Another spectacular case happens during the red tides caused by vertically migrating dinoflagellates. During these red tides, carbohydrate synthesis and its corresponding oxygen production takes place in the nutrient-depleted surface layer. Uptake of dissolved inorganic nitrogen (DIN) occurs in a deeper level of the water column, the nutricline, by using as energy source that provided by the carbohydrates previously synthesized in the surface layer. Consequently, during nutrient uptake there is no oxygen production. Redfield ratio anomalies for a red tide event were described in detail by Fraga *et al.* (1992).

Redfield ratio deviations can also be found in areas with denitrification and during *Trichodesmium* photosynthesis. Both cases, formerly recognised by Redfield *et al.* (1963) as special cases, are outside the limits of this paper.

The main objective of this paper is to present a new and useful approach to the relationship between $-\Delta O_2$, ΔN and ΔC , including a parameter ("NCO") which is unaffected by those cases where the Redfield ratio is not attained due to high synthesis of storage compounds and the subsequent remineralization in a deeper level in the water column. Therefore, this parameter, of general application for all oceanic and coastal environments, is a useful tool that provides the base needed for modelling purposes and tells us whether Redfield deviations are due to carbohydrates, lipids or both.

THEORY

Oxygen-Nutrient ratios

The ratios between oxygen consumption (or production) and regenerated (or assimilated) CO_2 and NO_3 are defined as

$$R_C = -\Delta O_2 / \Delta CO_2 \text{ and } R_N = -\Delta O_2 / \Delta NO_3$$

respectively.

For plankton with modified Redfield composition that include lipids: $R_C = 1.41$ and $R_N = 9.3$ (Laws, 1991, Anderson, 1995, Fraga *et al.* 1998). R_C is also known as the photosynthetic quotient (PQ).

When the Redfield ratio is not satisfied, the synthesis of biological material can be considered as the sum of two processes. One of them follows the Redfield ratio and the other one, which alters these ratios, corresponds to the synthesis of storage material.

According to the R_C and R_N definitions, the oxygen produced (ΔO_2) during the synthesis of Redfield matter is:

$$\Delta O_{2R} = -\Delta CO_{2R} \cdot R_C \quad (1)$$

$$\Delta O_{2R} = -\Delta NO_{3R} \cdot R_N \quad (2)$$

where the subindex R indicates the quantities of CO_2 and O_2 involved in photosynthesis, following Redfield.

The oxygen produced by the synthesis of storage material is:

$$\Delta O_{2s} = -\Delta CO_{2s} \cdot R_{Cs} \quad (3)$$

where the subindex s indicates the additional quantities of CO_2 and O_2 implicated in this additional synthesis. R_{Cs} is the equivalent to R_C for these storage substances.

The total O_2 produced and CO_2 consumed are:

$$\Delta O_2 = \Delta O_{2R} + \Delta O_{2s} \quad (4)$$

$$\Delta CO_2 = \Delta CO_{2R} + \Delta CO_{2s} \quad (5)$$

From 1 to 5, the total produced oxygen is:

$$\Delta O_2 = -\Delta NO_3 \cdot R_N (1 - R_{Cs} / R_C) - \Delta CO_2 \cdot R_{Cs} \quad (6)$$

Therefore, this equation fulfils all the requirements, independently of the elemental composition of

synthesized matter, and permits the calculation of the variations of oxygen, nutrients and CO₂; therefore, it allows us to obtain the net community production.

To establish equations 2 and 6, nitrate was considered as the only source of inorganic nitrogen. However, during photosynthesis, nitrite and especially ammonium are important inorganic nitrogen sources. Consequently, when these less oxidised forms of inorganic nitrogen are used, the produced oxygen will be lower. Therefore, the oxygen consumed during the regeneration processes of these nitrogen forms will also be lower. For this reason, it is necessary to make corrections to incorporate the nitrite and ammonium into equations 2 and 6 (Oudot, 1978; Ríos *et al.* 1989). The total oxygen produced is now:

$$\Delta O_{2\text{corr}} = -\Delta \text{DIN} \cdot R_N (1 - R_{\text{CS}}/R_C) - \Delta \text{CO}_2 \cdot R_{\text{CS}} \quad (7)$$

where

$$\Delta \text{DIN} = \Delta \text{NO}_3^- + \Delta \text{NO}_2^- + \Delta \text{NH}_4^+$$

and

$$\Delta O_{2\text{corr}} = \Delta O_2 - 0.5 \Delta \text{NO}_2^- - 2 \Delta \text{NH}_4^+$$

In places where precipitation or dissolution of CaCO₃ is important, a new correction must be incorporated into equation 7, which corrects CO₂.

$$\Delta O_{2\text{corr}} = -\Delta \text{DIN} \cdot R_N (1 - R_{\text{CS}}/R_C) - \Delta \text{CO}_{2\text{corr}} \cdot R_{\text{CS}} \quad (8)$$

where

$$\Delta O_{2\text{corr}} = \Delta \text{CO}_2 - 0.5(\Delta A + \Delta \text{NO}_3^- + 0.45 \Delta \text{NO}_2^- - \Delta \text{NH}_4^+)$$

and where ΔA introduces the alkalinity variation (Ríos *et al.*, 1989).

The “NCO” parameter

From the R_C and R_N definitions it follows that the quantity of oxygen produced (or consumed) plus carbon dioxide or nitrate consumed (or regenerated), multiplied by R_C or R_N respectively, is constant (Broecker, 1974).

$$“\text{CO}” = O_2 + R_C \cdot \text{CO}_2 \text{ and } “\text{NO}” = O_2 + R_N \cdot \text{NO}_3 \quad (9)$$

These constants are also characteristics for a given water mass (Broecker and Takahashi, 1981,

Minster and Boulahdid, 1987, Pérez *et al.*, 1993), if Redfield ratios are satisfied.

Consequently, when deviations of the ratio occur, integration of equation 7 yields:

$$“\text{NCO}” = O_{2\text{corr}} + R_N \cdot \text{DIN} (1 - R_{\text{CS}}/R_C) + R_{\text{CS}} \cdot \text{CO}_2 \quad (10)$$

where the integration constant “NCO” (Nitrate-CO₂-Oxygen) indicates the involved variables. If CO₂ is corrected by the precipitation or dissolution of CaCO₃, “NCO” became “NCAO” to indicate the introduction of alkalinity.

This “NCO” parameter, as with Broecker’s “CO” and “NO”, is independent of the photosynthesis and regeneration processes. If the CO₂ correction is used, it is also independent of precipitation or dissolution (chemical or biological) of CaCO₃. The parameter will only be affected by CO₂ and O₂ air-sea exchanges, N₂ fixation and denitrification. The advantage of “NCO” with regard to “CO” and “NO” is that R_C and R_N can be maintained fixed and equal to those of the modified Redfield composition, 1.41 and 9.3 respectively (Laws, 1991, Anderson, 1995 and Fraga *et al.* 1998). The deviations from the Redfield composition are incorporated into R_{CS} which can vary between 1 (carbohydrates) and 1.36 (lipids).

METHODS

Data from “Galicia IX” and “Galicia XI” cruises (Figueiras *et al.*, 1987; Castro *et al.*, 1994) are used in this study (Fig. 1). “Galicia IX” sampling was carried out in Ría de Vigo and adjacent shelf (NW of Spain) on board the R/V “García del Cid” on 3 October 1986. Coastal waters in the Eastern North Atlantic off Galicia (NW of Spain) were sampled during the “Galicia XI” on board the R/V “Investigador” between 9 and 14 May 1991. CTD SBE-19 with a rosette of 24 Niskin bottles of 1.7 litres were used at each station during “GALICIA XI”. Casts of 10 Niskin bottles of 1.7 litres supplied with three thermometers, two protected and one unprotected, were performed during “GALICIA IX”. Samples were taken from the surface every 10 meters to 60 m, and each 20 meters up to the bottom. The salinities were measured with a “Guildine-Autosal” salinometer. Nitrate, nitrite and ammonium were determined by colorimetric methods, using a Technicon autoanalyser (Hansen and Grasshoff, 1983; Mouriño

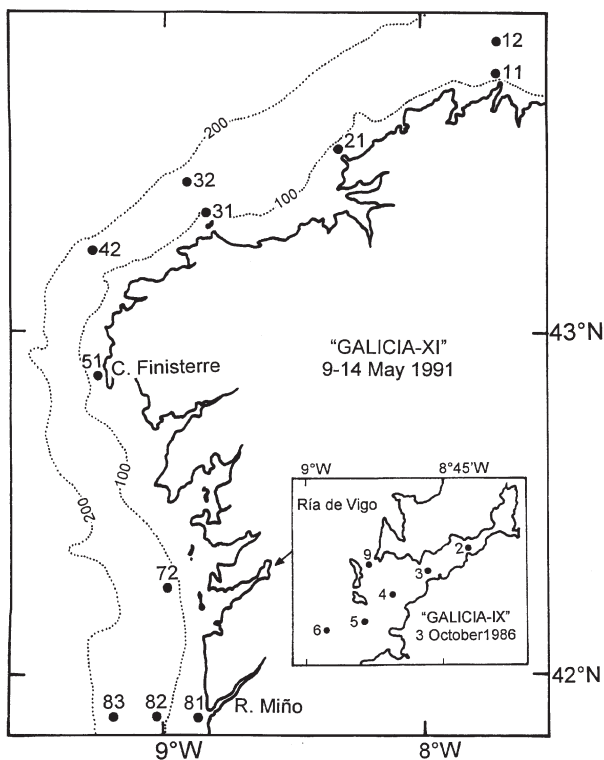


FIG. 1.- Sampling stations in the Ría de Vigo (Galicia IX) and in the Galician coastal shelf (Galicia XI).

and Fraga, 1985). The method has a shipboard precision for nitrate of $\pm 0.06 \mu\text{mol.kg}^{-1}$ (Castro and Salgado, 1996). CO_2 was calculated using equations of the carbonic system (Mehrbach *et al.*, 1973, Weis, 1974) from pH and alkalinity determinations which were analysed using potentiometric techniques (Pérez and Fraga, 1987a,b). A "Metrohm 654" pH meter with an Orion 81-04 electrode calibrated with 7.413 NBS buffer was used to determine pH. The method has a shipboard precision of ± 0.002 pH (Ríos and Rosón, 1996). The accuracy of ± 0.004 pH has been estimated using samples of Certified Reference Material (CRMs) provided by Dr. Dickson of University of California (Ríos and Rellán, in press). An automatic potentiometric titrator "Titrino Metrohm" was used to measure alkalinity with HCl to a final pH of 4.44. This method of determining alkalinity has a precision of 0.1% (Pérez and Fraga, 1987b), and the accuracy of $1.4 \mu\text{mol.kg}^{-1}$ was estimated from cross-calculation with measured CRMs (Ríos and Rellán, in press). The precision and accuracy of pH and alkalinity transmit $\pm 3 \mu\text{mol.kg}^{-1}$ to CO_2 . Dissolved oxygen

was analysed by the Winkler method using an automatic titration system "Metrohm 670" with platinum electrode. The precision of this method is $0.7 \mu\text{mol.kg}^{-1}$. For more details see Figueiras *et al.* (1987) and Castro *et al.* (1994).

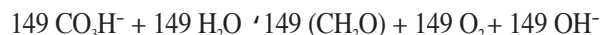
RESULTS

During the "Galicia IX" cruise an apparent red tide of *Gymnodinium catenatum* was observed in the interior of the Ría de Vigo and adjacent shelf (Figueiras and Pazos, 1991). A spring bloom of diatoms in the nutrient depleted surface waters was found in several coastal stations during the "Galicia XI" cruise (Castro *et al.*, 1994). In both cases deviations from Redfield ratios were observed.

Red tide

During a red tide, with a nutrient depleted surface layer, the migrating dinoflagellates synthesize carbohydrates in this surface layer during the light hours, and then take up nutrients at nutricline during the night. Carbohydrates, previously synthesized during the day, are used as energy source (Cullen, 1985, Fraga *et al.*, 1992).

In general, the process of synthesis carried out at the surface layer is:



and at the nutricline:

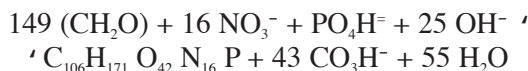


Figure 2 shows the relationship between dissolved inorganic nitrogen (DIN) and CO_2 at six stations where *Gymnodinium catenatum* was very abundant. The diatom *Skeletonema costatum* was also present, coexisting with the dinoflagellate population. The points where DIN was close to zero correspond to the surface layer with carbohydrate synthesis. The straight line with the ratio -16/43 indicates the synthesis taking place at the nutricline by dinoflagellates, while the diatom population follows the Redfield ratio line (16/106). The points situated between both lines correspond to samples where *G. catenatum* and *S. costatum* were coexisting.

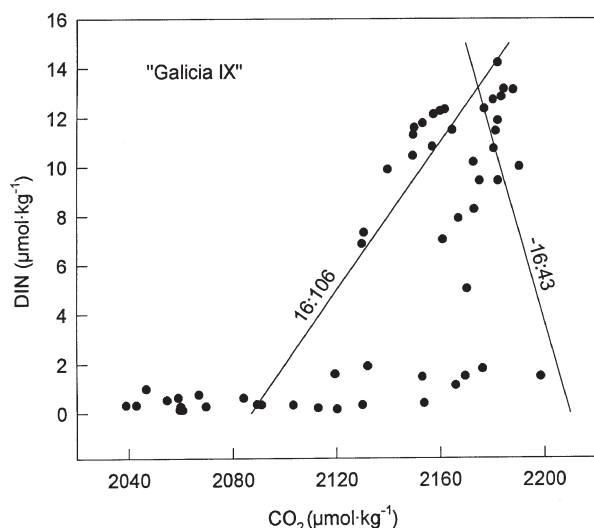


FIG. 2.- Relationship between total inorganic nitrogen (DIN) and CO_2 in six stations of "Galicia IX" cruise. Line 16:106 corresponds to the synthesis of organic matter by diatoms following Redfield. Line -16:43 indicates synthesis at nutricline by dinoflagellates.

Redfield deviations are reflected in the vertical profiles of "NO" and "CAO"; meanwhile "NCAO" remains constant with depth (Fig. 3). "NCAO" was calculated using equation 10. The value of $R_{CS} = 1$ was obtained fitting equation 7 with the experimental values corresponding to the sampled stations (fig. 1) from 0 to 10 meters, levels belonging to the same water body.

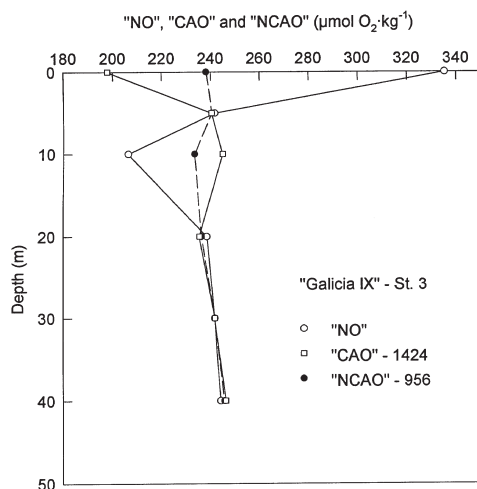


FIG. 3.- Vertical distribution of the chemical parameters "NO", "CAO" and "NCAO" during a *Gymnodinium catenatum* red tide at station 133 of "Galicia IX" cruise on 3 October 1986. The CO_2 was corrected for the precipitation or dissolution of CaCO_3 effects because the extensive cultivation of mussels rafts in the Ría de Vigo.

$$-\Delta\text{O}_{2\text{corr}} = \Delta\text{DIN}(2.68 \pm 0.63) + \Delta\text{CO}_2(1.00 \pm 0.04);$$

$$(r^2=0.99, n=17)$$

The obtained value $R_{CS} = 1$ means that carbohydrate synthesis was occurring at the surface layer.

Spring bloom of diatoms

Seven stations in the "Galicia XI" cruise, where the diatoms *Pseudo-nitzschia cf. seriata*, *Lauderia borealis*, *Schröderella delicatula* and *Chaetoceros* spp. were the more abundant species, showed nutrient depletion in the surface layer and Redfield ratio deviations. These deviations can be observed in the relationship between DIN and CO_2 (Fig. 4). In a similar way, as happened in the red tide case, the points close to zero DIN value correspond to surface samples where the uptake of CO_2 was incorporated presumably as carbohydrates. The points to the right of the 16/106 straight line (Redfield line) correspond to samples below the nutrient depleted surface layer where the remineralization of extra carbohydrates can give rise to extra inorganic CO_2 . However, another possible explanation could be the nitrogen assimilation at depth using the extra carbohydrates synthesized at surface as an energy source. According to Richardson and Cullen (1995) and Moore and Villareal (1996), diatoms with an excess of carbohydrates sink faster than those reflecting the Redfield composition. Once these diatoms reach a level with enough nutrients, they start to assimilate nitrogen. This diatom behaviour was found by Richardson and Cullen (1995) and Moore and Villareal (1996), in laboratory experiences where a faster sinking of diatoms with an excess of carbohydrates was also described.

The "NO" and "CO" profiles (Fig. 5) clearly indicate Redfield deviations can occur during spring blooms; however, the "NCO" remains almost constant along the whole profile. The slight deviation from the vertical is due to the air-sea gas exchange processes at the interface. The "NCO", as in the red tide case, was calculated using equation 10 with the value of R_{CS} ratio for carbohydrate synthesis ($R_{CS} = 1$), which was obtained by fitting equation 7 with the experimental data of the stations indicated in fig. 1

$$-\Delta\text{O}_{2\text{corr}} = \Delta\text{DIN}(2.76 \pm 1.51) + \text{DCO}_2(1.0 \pm 0.1);$$

$$(r^2=0.91, n=22)$$

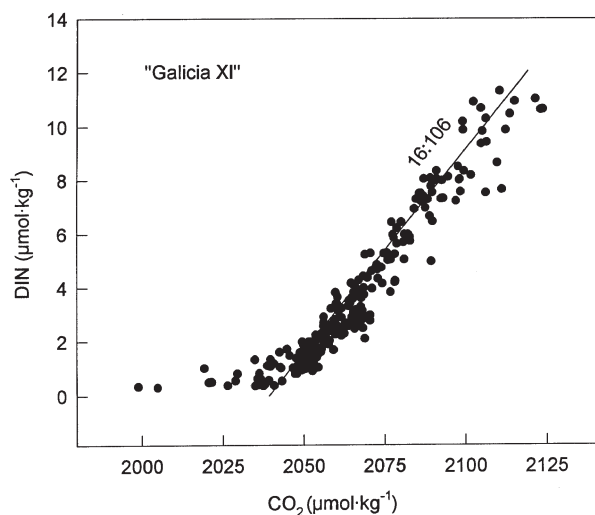


FIG. 4.- Relationship between total inorganic carbon (DIN) and CO_2 at seven stations of "Galicia XI" cruise. Line 16:106 indicates the synthesis following Redfield ratio.

Only data from surface to 20 meters were used not only to include only one water body, but also to avoid inclusion in the regression samples that fulfil the Redfield ratio because when that occurs, R_c is a function of R_N and vice versa, the matrix is indeterminate and the determinant is zero.

DISCUSSION

The new formulation given here allows us to deal adequately with cases where the Redfield composition is not satisfied. We showed two cases in the surface layer when assimilation processes were responsible for the Redfield deviations. Another case which is found in the water column, is that related to the differential remineralization of the sinking particles (Tanoue, 1985). Through equations 7 and 8, it is possible to calculate the oxygen or nutrient variations and therefore the net community production in a given water mass. On the other hand, the "NCO" parameter (equation 10) is very useful in water mass mixing models. According to the reversibility of the photosynthesis-remineralization processes, the "NCO" parameter (eq. 10) can be calculated from elemental composition of plankton or from inorganic nutrients and oxygen concentrations in seawater. The elemental composition of plankton presents a serious inconvenience because the dissolved organic matter produced during trophic interactions is excluded from the analysis of par-

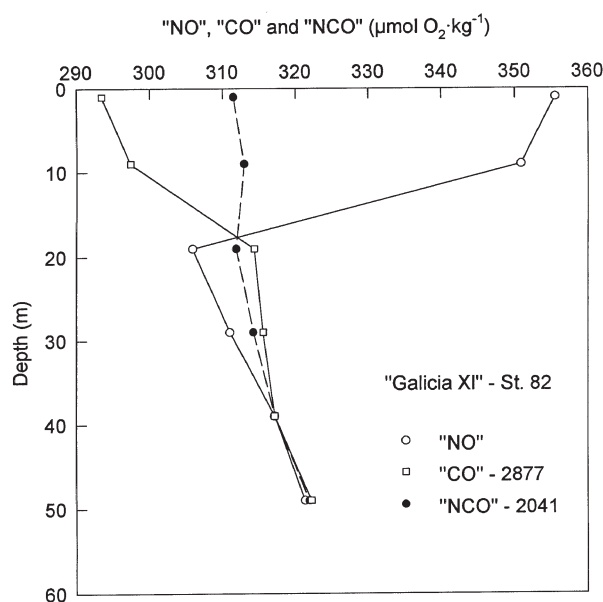


FIG. 5.- Vertical distribution of the chemical parameters "NO", "CO" and "NCO" during a spring bloom of diatoms (*Rhizosolenia delicatula*, *Chaetoceros socialis*, *Pseudo-nitzschia cf. seriata*, *Leptocylindrus danicus* and *minimus*) at station 82 of "Galicia XI" cruise on 14 May 1991.

ticulate matter. On the other hand, the chemical composition of plankton can vary considerably during the day (Cullen, 1985, Richardson and Cullen, 1995, Moore and Villareal, 1996). However, inorganic nutrients and oxygen concentrations have the advantage of integrating the history of the previous days, and due to their easier sampling and analysis facilities permit us also to cover a larger oceanographic area.

The accuracy of the "NCO" parameter was checked against "CO" and "NO" by means of triangular diagrams of the biochemical composition of the organic matter (Fraga *et al.*, 1998). In Figure 6, each side of the triangle represents the proportion of carbon in the three groups of biomolecules. The protein group with $R_c = 1.58$ contains phosphorus compounds and chlorophylls. Lipid and carbohydrate groups have $R_c = 1.36$ and $R_c = 1.00$, respectively. The modified Redfield composition (Laws, 1991, Anderson, 1995, Fraga *et al.*, 1998) including lipids (represented by the point inside the triangles in fig. 6) contains 45.1% of proteins, 12.1% of phosphorus compounds, 1.9% of chlorophylls, 16.6% of lipids and 24.4% of carbohydrates, by weight. When this mean composition is expressed in carbon, phosphorus compounds and chlorophylls are included in the protein group, the proportions are: 55.7% of

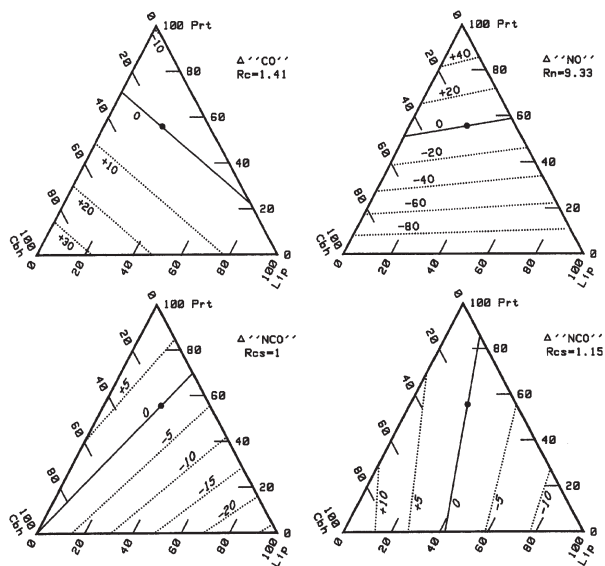


FIG. 6.- Oxygen errors (in percentage of moles) when is calculated from the synthesis or oxidation of particulate organic matter of different biochemical composition and by using “CO”, “NO” and “NCO”. Carbon proportion of the three main groups of biomolecules (carbohydrates, lipids and proteins) are indicated on each side of the triangles. The point inside the triangles represents the modified Redfield composition according to Anderson (1995) and Fraga *et al.* (1998).

total carbon in protein, 24.0% of lipids and 20.3% of carbohydrates. Representing the relative proportion of proteins by Prt, lipids by Lip and carbohydrates by Cbh inside the triangles, then $Prt+Lip+Cbh = 1$. Because each group is expressed in moles of carbon, the total oxidation of the particulate organic matter will produce $CO_2 = 1$ and $NO_3 = Prt / 3.69$, where 3.69 is the C/N ratio for proteins.

The moles of oxygen consumed during the oxidation, will be:

$$\Delta O_2 = 1.58 Prt + 1.36 Lip + 1.00 Cbh$$

where 1.58, 1.36 and 1.00 are the corresponding R_C .

The estimation of oxygen consumed by using equations (1) (“CO”), (2) (“NO”) and (6) (“NCO”) is:

- (1) ΔO_2 estimated = R_C
- (2) ΔO_2 estimated = $R_N Prt/3.69$
- (6) ΔO_2 estimated = $R_N Prt/3.69 (1 - R_{CS}/R_C) + R_{CS}$

Oxygen errors ($\&O_2$) are calculated according to:

$$\&O_2 = 100 (\Delta O_2 \text{ estimated} - \Delta O_2) / \Delta O_2$$

Figures 6a and 6b show the $\&O_2$ by using “CO” and “NO” assuming Redfield composition ($R_C = 1.41$ and $R_N = 9.3$). Figure 6c shows the $\&O_2$ by using “NCO” when Redfield deviations are due to carbohydrates ($R_{CS} = 1$). The use of “NCO” permits the estimate with higher accuracy of the oxygen consumed during the mineralisation of organic matter even when its composition does not follow Redfield ratios. “NO” (fig. 6b) shows the higher influence of Redfield deviations due to the variations of the C/N ratios. It is well known the ratio C/N increases with depth in the ocean. An oxygen anomaly using “NO” is about five times greater than that using “NCO”.

The previous discussion was constructed assuming that Redfield deviations are due to carbohydrates. However, deviations can be also due to a mixture of carbohydrates and lipids; therefore the R_{CS} value holds between 1 (carbohydrates) and 1.36 (lipids). By checking different R_{CS} values, we found that when the composition of organic matter is unknown or a high lipid contents is suspected as in coccolithophorid blooms and in polar waters, a R_{CS} value of 1.15 (fig. 6d) could give better results.

In summary, when $-\Delta O_2$, DNin, ΔCO_2 do not fulfil the Redfield ratios it is possible to establish the relationship between these variables by using the “NCO” parameter which is independent of those deviations. This chemical parameter remains invariable during photosynthesis and regeneration processes as happens with the “NO” and “CO” parameters. Including the oxygen correction (equation 7), it is also independent to the new and regenerated production. If alkalinity correction in CO_2 is made (equation 8), it became invariable to the precipitation or dissolution of calcium carbonate. The “NCO” parameter is only affected by CO_2 and O_2 air-sea exchanges, denitrification and fixation of molecular nitrogen by *Cyanophyceae*. On the other hand, since “NCO” is defined using inorganic nutrient variations, it is independent of whether the organic matter remains as particulate or dissolved material. It is also independent of the vertical transport of organic matter by sedimentation.

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REFERENCES

- Anderson, S.A. 1995.- On the hydrogen and oxygen content of marine phytoplankton. *Deep-Sea Research*, 42: 1675-1680.
- Banse, K. 1994.- Uptake of inorganic carbon and nitrate by marine plankton and the Redfield ratio. *Global Biogeochemical Cycles*, 8: 81-84.
- Broecker, W.S. 1974.- "NO", a conservative water-mass trace. *Earth and Planetary Science Letters*, 23: 100-107.
- Broecker, W.S. and T. Takahashi. 1981.- Hydrography of the central Atlantic - IV. Intermediate waters of Antarctic origin. *Deep-Sea Research*, 28A: 177-193.
- Castro, C.G. and X.A. Alvarez-Salgado. 1996.- *Nutrient measurements*. In *Recueil de données par Le Groupe CITHER-2*. Volume 3. Edited Laboratoire de Physique des Océans (96-02). Brest. France. Pags. 29-48.
- Castro, C.G., F.F. Perez, X.A. Alvarez-Salgado, G. Roson and A.F. Ríos. 1994.- Hydrographic conditions associated with the relaxation of an upwelling event off the Galician coast (NW Spain). *Journal of Geophysical Research*, 99: 5135-5147.
- Cullen, J.J. 1985.- *Diel vertical migration by dinoflagellates: Roles of carbohydrate metabolism and behavioral flexibility*. In: Rankin, M.A. (ed.) *Migration: mechanisms and adaptive significance*. Contrib. Marine Science (Suppl), 27: 135-152.
- Figueiras, F.G., R. Prego, F.F. Pérez, A.F. Ríos and F. Fraga. 1987.- Campaña "Galicia IX". Rías. *Datos Informativos Instituto de Investigaciones Marinas*, 21: 130 pp.
- Figueiras, F.G. and Y. Pazos. 1991.- Hydrography and phytoplankton of the Ría de Vigo before and during a red tide of *Gymnodinium catenatum* Graham. *Journal of Plankton Research*, 13: 589-608.
- Fraga, F., F.F. Perez, F.G. Figueiras and A.F. Ríos. 1992.- Stoichiometric variations of N, P, C and O₂ during a *Gymnodinium catenatum* red tide and their interpretation. *Marine Ecology Progress Series*, 87: 123-134.
- Fraga, F., A.F. Ríos, F.F. Perez and F.G. Figueiras. 1998. Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and the mineralisation of the organic matter in the sea. *Scientia Marina*, 62(1-2): 161-168.
- Hansen, H.P. and Grasshoff, K., 1983.- *Automated Chemical Analysis*. In: K. Grasshoff, M. Ehrhardt and K. Kremlig (Editors), *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, 419 pp.
- Laws, E.A. 1991.- Photosynthetic quotients, new production and net community production in the open oceans. *Deep-Sea Research*, 38: 143-167.
- Mehrbach, C., C.H. Culberson, J.E. Hawley and R.M. Pytkowicz. 1973.- Measurements of the apparent dissociation constant of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography*, 18: 897-907.
- Minster, J.F. and M. Boulhadid. 1987.- Redfield ratios along isopycnal surfaces - a complementary study. *Deep-Sea Research*, 34: 1981-2003.
- Moore, J.K. and T.A. Villareal. 1996.- Buoyancy and growth characteristics of three positively buoyant marine diatoms. *Marine Ecology Progress Series*, 132: 203-213.
- Mouriño, C. and F. Fraga, F. 1985.- Determinación de nitratos en agua de mar. *Investigación Pesquera*, 49: 81-96.
- Oudot, C. 1978. Intérêt du concept NO (oxygène corrigé de la respiration) pour l'étude de l'écosystème de l'upwelling équatorial. *Cah. ORSTOM, sér. Océanogr.*, 16(2): 191-199.
- Pérez, F.F. and F. Fraga. 1987a.- The pH measurements in seawater on NBS scale. *Marine Chemistry*, 21: 315-327.
- Pérez, F.F. and F. Fraga. 1987b.- A precise and rapid analytical procedure for alkalinity determination. *Marine Chemistry*, 21: 169-182.
- Pérez, F.F., C. Mouriño, F. Fraga, A.F. Ríos. 1993.- Displacement of water masses and remineralization rates off the Iberian peninsula by nutrient anomalies. *Journal of Marine Research*, 51: 869-892.
- Redfield, A.C., B.H. Ketchum and F.A. Richards. 1963.- *The influence of organisms on the composition of sea-water*. pp.26-77. in M.N. Hill ed. *The Sea*. Vol.2, pp.554. John Wiley & Sons, New York.
- Richardson, T.L. and J.J. Cullen. 1995.- Changes in buoyancy and chemical composition during growth of a coastal marine diatom: ecological and biogeochemical consequences. *Marine Ecology Progress Series*, 128: 77-90.
- Ríos, A.F., F. Fraga and F.F. Pérez. 1989.- Estimation of coefficients for the calculation of "NO", "PO" and "CO", starting from the elemental composition of natural phytoplankton. *Scientia Marina*, 53: 779-784.
- Ríos, A.F. and Rellán T.- *pH and alkalinity measurements*. In *Recueil de données par Le Groupe CITHER-3*. Volume 3. Edited Laboratoire de Physique des Océans (97-02). Brest. France. In press.
- Ríos, A.F. and Rosón, G., 1996.- *pH and alkalinity measurements*. In *Recueil de données par Le Groupe CITHER-2*. Volume 3. Edited Laboratoire de Physique des Océans (96-02). Brest. France. pags. 64-70.
- Sambrotto, R.N., G. Savidge, C. Robinson, P. Boyd, T. Takahashi, D.M. Karl, C. Langdon, D. Chipman, J. Marra and L. Codispoti. 1993.- Elevated consumption of carbon relative to nitrogen in the surface ocean. *Nature*, 363: 248-250.
- Tanoue, É. 1985.- Distribution and chemical composition of particulate organic matter in the Pacific sector of the Antarctic Ocean. *Transactions of the Tokyo University of Fisheries*, 6: 43-57.
- Weiss, R.F. 1974.- Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry*, 2: 203-215.

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