

Redfield ratios revisited: Removing the biasing effect of anthropogenic CO₂

Abstract—Redfield ratios of remineralization are calculated based on chemical data analysis on isopycnal surfaces. The concentrations of dissolved inorganic carbon used in this study were corrected for the anthropogenic CO₂ content as estimated with a back-calculation technique. The corrections increased the apparent carbon remineralization by 25–30%, thus proving important for the reliable estimation of Redfield carbon ratios in the presence of anthropogenic CO₂. Best estimates from this study largely confirm the more recently published Redfield ratios of remineralization. The following results were obtained for the latitude range 3–41°N along 20–29°W in the Northeast Atlantic Ocean: C_{org}:P ratio = 123 ± 10; C_{org}:N ratio = 7.2 ± 0.8; –O₂:C_{org} ratio = 1.34 ± 0.06; –O₂:P ratio = 165 ± 15; N:P ratio = 17.5 ± 2.0. These ratios are in close agreement with the average composition of phytoplankton and represent respiration of organic matter consisting on average of 52% protein, 36% polysaccharide, and 12% lipid.

Ratios of biorelevant elements in the ocean—the so-called Redfield ratios—have since the original publication of Redfield and coworkers (Redfield et al. 1963), proven a robust paradigm for understanding biogeochemical cycles in the ocean. Innumerable publications have made use of Redfield ratios, ranging from the estimation of new production on the basis of nitrate supply to the euphotic zone (Eppley and Peterson 1979) to the definition of new conservative tracers (e.g., Broecker 1974). Although substantial deviations from Redfield stoichiometry associated with biological production have been reported on shorter time- or regional scales (Sambrotto et al. 1993; Körtzinger et al. 2001), measurements of the composition of suspended organic particles in the ocean (Copin-Montegut and Copin-Montegut 1983) and of deep-water remineralization products (e.g., Takahashi et al. 1985; Minster and Boulahdid 1987; Anderson and Sarmiento 1994; Shaffer et al. 1999) have generally confirmed the Redfield ratios on a long-term and a large-scale basis.

Given this strong interest, a number of studies have been carried out to determine Redfield ratios from correlated changes in nutrient and oxygen abundances in the interior of the ocean. Although there is some conflicting evidence from these assessments (such as on the question of differential remineralization with depth), there is general agreement that some modifications of the original Redfield ratios are necessary. In particular, the Redfield –O₂:P ratio of 138, which was based on a stoichiometric model rather than an empirical relationship, was revised to 170 on the basis of nutrient and oxygen data (Takahashi et al. 1985; Anderson and Sarmiento 1994). Although more recent studies avoid pitfalls associated with the treatment of water mass mixing (neutral versus isopycnal surfaces, small-scale mixing, etc.), one obvious and significant source of uncertainty has not been addressed adequately—the bias of the carbon Redfield ratios due to the presence of anthropogenic CO₂. Previously, analyses were performed in areas where anthropogenic CO₂

was assumed (and hoped) to be absent (e.g., Pacific Ocean, Shaffer et al. [1999]), or Redfield carbon ratios were reported, noting that they were likely biased because of the presence of unknown amounts of anthropogenic CO₂ (Takahashi et al. 1985). Thus, the Redfield carbon ratios were least well determined.

Along isopycnals, the anthropogenic CO₂ burden decreases equatorward from the outcrops in high latitudes. Hence, concentrations of total dissolved inorganic carbon (C_T) along isopycnals depend not only on mixing of water with different preformed concentrations and biologically mediated carbon releases, but also on the time it was last ventilated (i.e., the time its anthropogenic CO₂ content was determined). Even if end-member mixing is properly accounted for, the observed C_T change along an isopycnal is the combination of respirative carbon release and the change in preformed anthropogenic CO₂ concentration. To extract the pure remineralization signal, the masking effect of anthropogenic CO₂ has to be eliminated.

Here, we use estimates of the anthropogenic carbon content to correct measured C_T values to preanthropogenic conditions. We then estimate Redfield ratios following the approaches of Takahashi et al. (1985) and Minster and Boulahdid (1987). The analysis was restricted to the North Atlantic Ocean, where the deepest penetration of anthropogenic CO₂ is found (Körtzinger et al. 1998; Wanninkhof et al. 1999), and hence, the strongest bias can be expected. The resulting Redfield carbon ratios are discussed from a biogeochemical perspective.

Materials and methods—Data: Our analysis was performed using data from a meridional section along 20–29°W in the North Atlantic Ocean ([OACES] Ocean Atmosphere Carbon Exchange Study, 4 July–30 August 1993, <http://www.aoml.noaa.gov/ocd/oaces/>, accessed December 1999). The technique of Takahashi et al. (1985) further required a data set in the South Atlantic, where we made use of the meridional section along 25°W (heading toward 36°W/54°S south of 35.5°S) sampled during the South Atlantic Ventilation Experiment (SAVE, legs 5 and 6); data provided by Carbon Dioxide Information Analysis Center, Oak Ridge, Tennessee.

Redfield ratios: Redfield ratios were calculated following two approaches, both of which are based on data analysis on isopycnal surfaces and which differ mainly in the way mixing end-members are determined. The common idea is to examine concurrent changes in nutrient and oxygen concentrations along isopycnal surfaces. If end-member mixing and preformed concentrations are properly quantified, ratios of residual concentration changes should directly reflect the Redfield ratios of remineralization. Although certain deficiencies in the treatment of mixing and the choice of end members have been identified in both techniques, they produce reasonable estimates of Redfield ratios if confined to

Table 1. Estimated properties of the northern and southern end members (comma-separated) of isopycnals $\sigma_\theta = 27.00, 27.10,$ and $27.20,$ as calculated following the approach of Takahashi et al. (1985).

Isopycnal	θ^o	O ₂ ^o	NO ₃ ^o	PO ₄ ^o	A _T ^o	C _T ^o	Corrected C _T ^o
27.00	13.2, 5.2	255, 308	5.1, 20.2	0.15, 1.36	2355, 2277	2104, 2117	2068, 2052
27.10	12.2, 3.1	261, 324	7.0, 24.9	0.42, 1.65	2348, 2275	2112, 2121	2070, 2055
27.20	11.2, 1.8	266, 335	7.8, 27.3	0.57, 1.81	2347, 2274	2117, 2128	2070, 2065

ocean domains of subbasin scale. Both techniques, outlined very briefly below, were applied using measured C_T values as well as C_T values corrected to preanthropogenic conditions by subtracting the estimated anthropogenic CO₂ content.

According to the method of Takahashi et al. (1985)—hereafter referred to as TBL85—the linear correlation lines between oxygen and potential temperature are extrapolated toward the saturation curve for oxygen. The intersection points provide values for the end-member temperature and oxygen concentration. The end-member concentrations of other nutrients are then deduced from the linear oxygen–nutrient relationships. Table 1 shows resulting end-member values for the TBL85 approach, which generally agree very well with those given by Takahashi et al. (1985). The proportions of northern and southern end-member components are calculated on the basis of the potential temperature. Using these proportions and the end-member concentrations, conservative mixing values (i.e., values that should be present only if they were affected by two-end-member–mixing along isopycnals) can be calculated for all nutrients. Redfield ratios are then calculated from deviations of measured from conservative mixing values. Here, the OACES data set (domain: 21–41°N) was used to calculate northern end-member values, and the SAVE data set (domain: 25–45°S) provided estimates of southern end-member values. The analysis was only feasible on the isopycnals $\sigma_\theta = 27.00, 27.10,$ and 27.20 in the North Atlantic Ocean. In order to retain linear oxygen–property relationships, the analysis could not be extended further south.

According to the method of Minster and Boulahdid (1987)—hereafter referred to as MB87—the assumption of two-end-member–mixing is tested by examining the salinity–NO relationship, where NO is a conservative water mass tracer (Broecker 1974). In modification of the original definition of NO, we used the following equation.

$$\text{NO} = 9 \cdot [\text{NO}_3^-] - \text{AOU}$$

AOU is the apparent oxygen utilization calculated as the difference between saturation oxygen concentration and measured oxygen concentration. End-member concentrations are selected at the extremes of the salinity versus NO plots, thereby making sure that those data points are also located at the geographical borders of the data domain. Like in TBL85, Redfield ratios were calculated from differences between measured and calculated mixed values. The MB87 approach was applied on the OACES data set (domain: 3–41°N) for the isopycnals $\sigma_\theta = 27.00, 27.10, 27.20, 27.30,$ and 27.40 in the North Atlantic Ocean. The larger domain was required to extend the analysis to the deeper isopycnals $\sigma_\theta = 27.30$ and $27.40,$ which exhibit smaller remineraliza-

tion signals. On all chosen isopycnals, the observed linear NO–salinity relationship allowed the application of a two-end-member–mixing model. Note that by choosing the end-member values at the borders of the domain, this technique eliminates the need for a southern Atlantic data set to provide the southern end member.

The domain covered by our analysis (3–41°N, 200–900 m deep) is dominated by Mode Waters of northern origin, which are part of the anticyclonic recirculation south of the North Atlantic Current (McCartney and Talley 1982). Of these, the subpolar variety of the Eastern North Atlantic Water (ENAW_p) forming north of ~40°N and moving southward (Pollard et al. 1996; Castro et al. 1998) is the most important. On the shallowest isopycnal, $\sigma_\theta = 27.00$ ($\theta > 12.5^\circ\text{C}$ north of 20°N), the subtropical variety (ENAW_T) that forms south of 40°N dominates. Deeper isopycnals show southwardly increasing influence of Antarctic Intermediate Water (AAIW). At the southern border, isopycnals $\sigma_\theta = 27.30$ and 27.40 border the core of this low-salinity AAIW tongue (Tsuchiya et al. 1992), which extends to 22°N at northwardly increasing densities (and depths). North of 22°N, direct mixing of AAIW with Mediterranean Sea Outflow Water (MSW) occurs at isopycnals below the domain of this analysis. Thus the MSW core around $\sigma_\theta = 27.70$ (Tsuchiya et al. 1992) poses a major limit for the present analysis, because here, the simple two-end-member–mixing model is not applicable. In essence, the chosen domain can be regarded as a mixing regime with the two end members ENAW_p and AAIW.

Speer (1997) demonstrated that diapycnal mixing is weak (indistinguishable from zero) in the thermocline ($\sigma_\theta = 26.6$ – 27.6) of the North Atlantic Ocean. Furthermore, the area investigated is not influenced by boundaries, passages, or events that might give rise to strong cross-isopycnal mixing. On the other hand, Klein and Tomczak (1994) found evidence for unidirectional diapycnal mixing in the front between North and South Atlantic Central Water (NACW and SACW near 15°N on our section), which they attributed to double diffusion. This effect, however, decreased with depth and probably only marginally affects our shallow isopycnals ($\sigma_\theta = 27.00$ and 27.10) found at depths of 350–500 m in this area. We therefore think that the rather simplistic isopycnal mixing approach used in TBL85 and MB87 is justified here.

Anthropogenic CO₂: Anthropogenic CO₂ was determined using a back-calculation technique published independently by Brewer (1978) and Chen and Millero (1979), which involves quantification of biologically mediated changes in the marine CO₂ system to reveal any difference between a sample's preformed content of total dissolved inorganic carbon (C_T) and corresponding contemporary preformed C_T values.

Table 2. Redfield ratios of remineralization. Results represent ratios of changes in nitrate, phosphate, total dissolved inorganic carbon (C_T), and dissolved oxygen along isopycnal surfaces in the North Atlantic Ocean as calculated following the approaches of Takahashi et al. (1985), herein TBL85, and Minster and Bouhladid (1987), herein MB87. All C_T values were corrected to preanthropogenic conditions by subtracting estimated concentrations of anthropogenic CO_2 . Results obtained using uncorrected C_T values are given in brackets.

Isopycnal	Depth range (m)	N:P	$C_{org}:P$	$-O_2:P$	$C_{org}:N$	$-O_2:N$	$-O_2:C_{org}$
TBL85							
27.00	200–500	14.4±0.7	102±12(72±9)	127±12	7.2±0.4(5.1±0.3)	9.1±0.3	1.31±0.04(1.82±0.04)
27.10	330–580	16.1±0.9	123±7(85±6)	158±11	7.6±0.3(5.2±0.3)	9.9±0.3	1.32±0.02(1.92±0.08)
27.20	500–680	16.8±1.3	131±18(86±9)	165±19	7.8±0.5(5.1±0.2)	10.1±0.3	1.31±0.03(1.99±0.07)
MB87							
27.00	200–500	15.7±1.8	101±14(87±20)	136±20	6.8±0.2(5.5±0.4)	9.0±0.3	1.31±0.03(1.64±0.05)
27.10	330–580	18.6±1.1	123±7(100±9)	167±13	6.8±0.2(5.5±0.2)	9.3±0.2	1.34±0.03(1.69±0.04)
27.20	500–680	19.2±1.3	126±10(104±10)	175±15	6.5±0.2(5.1±0.2)	9.1±0.2	1.38±0.03(1.78±0.06)
27.30	620–760	17.6±2.0	116±15(93±21)	167±22	6.5±0.5(5.1±0.5)	9.2±0.4	1.40±0.04(1.82±0.10)
27.40	710–920	18.0±2.3	113±18(81±20)	165±23	6.5±0.4(4.7±0.5)	9.4±0.4	1.43±0.03(2.04±0.11)

The potential of the back-calculation approach of providing model-independent fossil fuel CO_2 uptake estimates has been demonstrated by several authors (e.g., Jones and Levy 1981; Chen 1987; Brewer et al. 1997; Körtzinger et al. 1998).

The back-calculation requires quantification of changes in the marine CO_2 system due to decomposition of particulate organic matter, dissolution of particulate carbonates, and mixing after a water parcel leaves contact with the atmosphere. This is feasible on the basis of measurements of total alkalinity (A_T), C_T , oxygen, salinity, and potential temperature (θ). A detailed description of the method and its major drawbacks can be found in Körtzinger et al. (1998). Contemporary preformed values were calculated using either published θ -property relationships (A_T^0 , North Atlantic: Millero et al. 1998) or θ -property relationships calculated from published surface data (C_T^0 , North Atlantic: Johnson et al. 1999), or from surface samples covering the full range of potential temperatures (A_T^0 , C_T^0 , South Atlantic: SAVE data). The a priori choice of a depth-independent $-O_2:C_{org}$ ratio of 1.35 for the back-calculation was justified a posteriori by our results (described below).

The overall uncertainty of the anthropogenic CO_2 has been estimated to be $10 \mu\text{mol kg}^{-1}$. There is, however, the potential for a systematic error of the same size from the use of summer values for calculating present-day preformed C_T instead of winter values, as already pointed out by Chen and Pytkowicz (1979). Using the same OACES data set, Wanninkhof et al. (1999) report that this back calculation technique seems to slightly overestimate the penetration of anthropogenic CO_2 into the North Atlantic. On the other hand, Wanninkhof et al. (1999) showed that the more recent technique of Gruber et al. (1996) underestimated anthropogenic CO_2 penetration in the north. However, the two different techniques yielded inventories of anthropogenic CO_2 that agree within 20%. By choosing the older back-calculation technique, we likely place an upper limit on the anthropogenic CO_2 -related correction of the Redfield carbon ratios. It should be pointed out that Redfield carbon ratios are sensitive only to the isopycnal gradient in anthropogenic CO_2 , rather than to its absolute concentrations. Hence, any systematic errors—such as is potentially introduced by calcu-

lating present-day preformed C_T from summer values—cancel out as long as they represent a constant offset. A relative error of 20% in estimated anthropogenic CO_2 concentrations results in a 3–11% (average 7%) change in the Redfield carbon ratios, depending on the isopycnal and the technique (TBL85 or MB87).

Results and discussion—Anthropogenic CO_2 showed highest concentrations in the north (41°N), decreasing with increasing depth from around $34 \mu\text{mol kg}^{-1}$ on $\sigma_\theta = 27.00$ to $\sim 24 \mu\text{mol kg}^{-1}$ on $\sigma_\theta = 27.40$. At the southern border of the MB87 domain (3°N), a similar trend with depth from $\sim 28 \mu\text{mol kg}^{-1}$ ($\sigma_\theta = 27.00$) to $\sim 16 \mu\text{mol kg}^{-1}$ ($\sigma_\theta = 27.40$) was observed. A distinct minimum in anthropogenic CO_2 levels was found around 15°N , ranging from around $9 \mu\text{mol kg}^{-1}$ ($\sigma_\theta = 27.00$) to $\sim 7 \mu\text{mol kg}^{-1}$ ($\sigma_\theta = 27.40$). The difference in anthropogenic CO_2 concentrations between the 41°N and 15°N accounts for 25–30% of the observed isopycnal C_T gradient in the same region ($60\text{--}100 \mu\text{mol kg}^{-1}$). At the southern border of the TBL85 domain (21°N) estimates of anthropogenic CO_2 range between $12 \mu\text{mol kg}^{-1}$ ($\sigma_\theta = 27.00$) and $10 \mu\text{mol kg}^{-1}$ ($\sigma_\theta = 27.20$). Here, anthropogenic CO_2 accounted for 38–46% of the apparent change in C_T along the isopycnals. In both domains, the along-isopycnal gradient in anthropogenic CO_2 was a substantial portion of the C_T gradient and, thus, biased Redfield carbon ratio estimates significantly.

Estimated Redfield ratios are summarized in Table 2. All carbon ratios are reported corrected as well as uncorrected for anthropogenic CO_2 . Good agreement in calculated Redfield ratios was generally found between the TBL85 and the MB87 approaches, and the significantly different ways of choosing end-members do not appear to be critical here. In all cases, the correction causes a considerable increase in the ratios. Generally, the errors—as determined by the error of the slope of the property–property correlations—are smallest for the $\sigma_\theta = 27.10$ isopycnal and increase with depth as observed remineralization signals decrease.

The results indicate an increase in the $X:P$ ratios ($X = N, C, -O_2$) with depth between 200 and 680 m (isopycnals $\sigma_\theta = 27.00\text{--}27.20$), which is not observed in the other ratios.

The observed increase of the $-O_2:P$ ($C_{org}:P$) ratio from around 130 (100) to 165 (125) is in very good agreement with Shaffer et al. (1999), who found the $-O_2:P$ ($C_{org}:P$) ratio to increase with depth in the upper thermocline from ~ 140 (100) to ~ 170 (130). For the calculation of (error-weighted) means of the $X:P$ ratios (Fig. 1), we excluded the shallowest isopycnal $\sigma_\theta = 27.00$ because of this different signature.

We first compare our Redfield ratios with some prominent published results (Fig. 1). We found $-O_2:C_{org}$ ratios of 1.32 ± 0.03 (TBL85) and 1.36 ± 0.05 (MB87) using corrected C_T data. Without correction, these ratios are 1.78 ± 0.06 (TBL85) and 1.72 ± 0.15 (MB87), which seem even more biased high than the Takahashi et al. (1985) $-O_2:C_{org}$ ratio of 1.70 (based on TTO data). This is as expected, since the fossil fuel CO_2 gradient along the isopycnals at the time of OACES (1993) has increased since the time of TTO (1981). Clearly, the correction brings the $-O_2:C_{org}$ ratio much more in line with the original Redfield value of 1.30 (Redfield et al. 1963). Anderson and Sarmiento (1994) used an $-O_2:C_{org}$ ratio of 1.45, which was not determined from water column data but represented the mean of the original Redfield value of 1.30 and an $-O_2:C_{org}$ ratio of 1.60 measured on organic detritus (Martin et al. 1987). However, Anderson and Sarmiento (1994) point out that the Martin et al. (1987) value for detritus seems to be an overestimate and has to be regarded as an upper limit. This is confirmed by our results. It is interesting to note that much of the scatter in the uncorrected C_T -oxygen correlations was removed when C_T values corrected for anthropogenic CO_2 were used, yielding especially small errors for the $-O_2:C_{org}$ ratio.

Our $C_{org}:P$ ratios of 124 ± 8 (TBL85) and 122 ± 12 (MB87) are in close agreement with the estimate of Anderson and Sarmiento (1994). $C_{org}:P$ ratios based on uncorrected C_T data are 85 ± 13 (TBL85) and 99 ± 15 (MB87). Takahashi et al. (1985) state that their value of 95 is an underestimate. By putting upper and lower limits on the ratio, they give a best estimate of 117 ± 21 , which seems very reasonable in the light of the present findings.

The mean $-O_2:P$ ratio of 165 ± 15 agrees well with the Anderson and Sarmiento (1994) value of 170 ± 10 , as well as Broecker et al. (1985), who found values of 165 ± 7 and 172 ± 6 in the North Atlantic Ocean. However, the $-O_2:P$ ratio (as do all phosphorus Redfield ratios) indicates differential remineralization in the upper thermocline, as discussed above.

Means of the $N:P$ and $C_{org}:N$ ratio are 17.5 ± 2.0 and 7.2 ± 0.8 , respectively. Again, the correction for anthropogenic CO_2 shifted the $C_{org}:N$ ratios upward from ratios close to the Takahashi et al. (1985) ratio of 5.6. The nitrogen ratios after TBL85 and MB87 show larger differences between the two techniques. This discrepancy is due to the increase of the domain in MB87 ($3-41^\circ N$) versus TBL85 ($21-41^\circ N$). The results in the larger MB87 domain can be split into a northern and a southern region at $17^\circ N$, roughly coinciding with the front between NACW and SACW. Both subregions show much tighter property-property relationships than the region as a whole. The resulting $N:P$ and $C:N$ ratios are significantly different between these subregions (Fig. 2). In all cases, the northern region ($17-41^\circ N$) yields nitrogen ra-

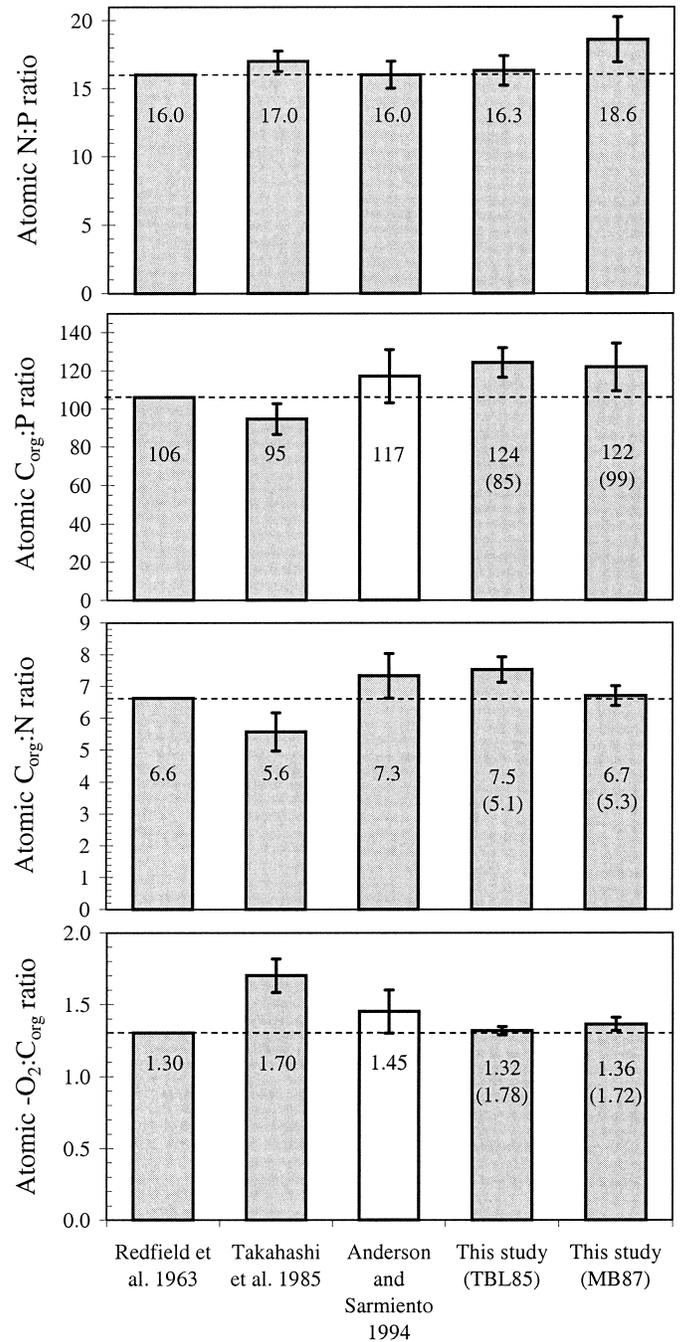


Fig. 1. Comparison of the results of this study with published Redfield ratios of remineralization. Shown are the carbon ratios ($C_{org}:P$, $C_{org}:N$, $-O_2:C_{org}$), which are subject to bias because of the presence of anthropogenic CO_2 . All ratios were calculated using C_T values corrected to preanthropogenic conditions by subtracting estimated concentrations of anthropogenic CO_2 . Values in brackets show the results obtained using uncorrected C_T values. Anthropogenically unaffected $N:P$ ratios are shown for comparison. Note that the $-O_2:C_{org}$ ratio of 1.45 ± 0.15 after Anderson and Sarmiento (1994) was not determined from water column data but represents the mean of the original Redfield et al. (1963) value of 1.30 and an $-O_2:C_{org}$ ratio of 1.60 for organic detritus (Martin et al. 1987). Using this ratio and their well-constrained $-O_2:P$ ratio of 170, they obtained the $C_{org}:P$ ratio of 117 ± 14 .

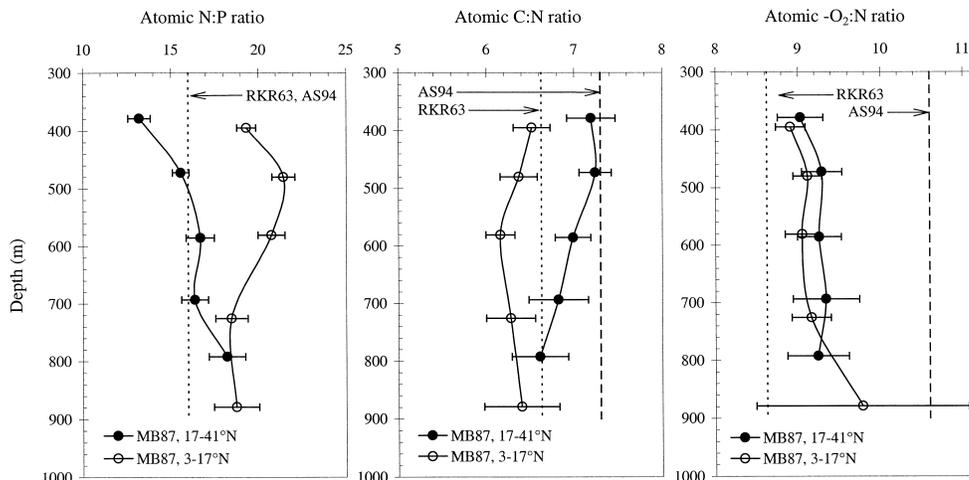


Fig. 2. Results for the N:P, C:N, and $-O_2:N$ ratios on all isopycnals ($\sigma_\theta = 27.00\text{--}27.40$) after MB87, shown separately for the northern (17–41°N) and southern subregion (3–17°N). Also shown are the mean ratios after Redfield et al. (RKR63, 1963) and Anderson and Sarmiento (AS94, 1994).

tios that agree well with the results after TBL85 for the region 21–41°N. The southern subregion (3–17°N) has much higher (lower) N:P (C:N) ratios on the shallow isopycnals, whereas both subregions are statistically indistinguishable on the deep isopycnal $\sigma_\theta = 27.40$. The similar behavior of the $-O_2:N$ ratio is not significant. One possible explanation for this regional pattern is an additional (relative to phosphorus)

low-latitude input of nitrate from sources such as nitrogen fixation. This is in line with Carpenter and Romans (1991) and Carpenter et al. (1999), who showed examples of nitrogen fixation as an important source of new N for the tropical Atlantic Ocean. On the other hand, our findings do not support the results of Gruber and Sarmiento (1997, *see fig. 13b*), who found enhanced nitrogen fixation in the northern rather than the southern subregion. Given the limitations of the present data set, we cannot solve this paradox here. Our results do, however, support the notion that this important question does not seem to be fully answered yet and requires further work.

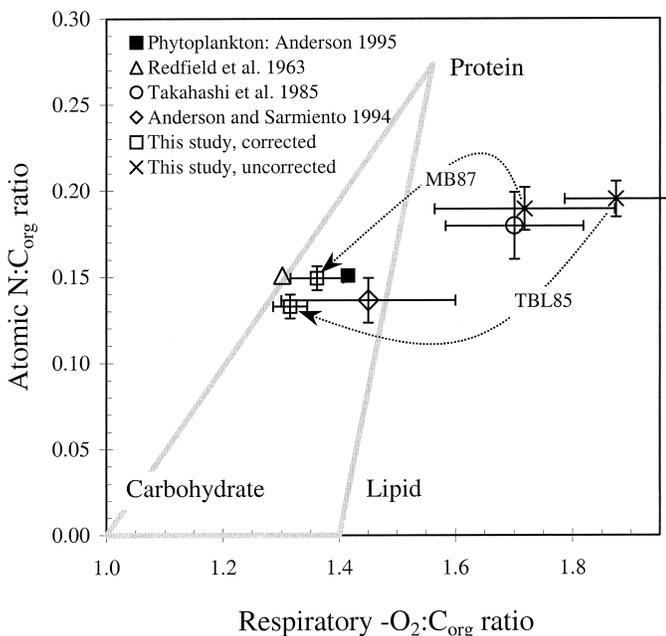


Fig. 3. Plot of the $-O_2:C_{org}$ ratio of respiration versus the N: C_{org} ratio showing results from this study and from prominent publications. The arrows indicate the effect of the correction for anthropogenic CO_2 in both techniques. Also shown are typical values for the mean composition of phytoplankton (Anderson 1995). The triangle spans the range of possible composition resulting from any mixture of the three major classes of organic constituents (Anderson 1995) of marine organic matter: protein (containing 4% nucleic acids), lipid, and polysaccharides.

In a second step, we plotted the respiratory $-O_2:C_{org}$ ratio versus the N: C_{org} ratio of different types of organic matter (Fig. 3) in order to examine our results in terms of chemical composition. A triangular area of possible composition can be defined by using “end-members” (Anderson 1995) for the three classes of organic constituents: lipid ($C_{40}H_{74}O_5$), carbohydrate ($C_6H_{10}O_5$), and protein ($C_{3.83}H_{6.05}O_{1.25}N$). Note that in accordance with Anderson (1995), we assumed a 4% contribution from nucleic acids ($C_{9.625}H_{12}O_{6.5}N_{3.75}P$) to calculate the protein end-member. Any combination of these substances should be characterized by N: C_{org} and $-O_2:C_{org}$ ratios within the triangle. From this perspective, it is clear that the high $-O_2:C_{org}$ ratio of 1.70 of Takahashi et al. (1985) cannot be explained in biogeochemical terms. The results obtained here using uncorrected C_T values are even further off the triangular area revealing the steepening of the isopycnal gradient of anthropogenic CO_2 since the time of TTO. Also, the value of 1.45 ± 0.15 for the $-O_2:C_{org}$ ratio of Anderson and Sarmiento (1994) likely represents an upper limit for the chemical composition of organic matter. This provides additional evidence of an overestimation of the $-O_2:C_{org}$ ratio of 1.60 by Martin et al. (1987), which was used to yield the value of 1.45. In contrast, after correcting for anthropogenic CO_2 biases, results are well within the triangle as are values for the average composition of marine phytoplankton (Anderson 1995).

Our results correspond to respiration of organic matter consisting of ~52% protein, 36% carbohydrate, and 12% lipid (0.5% of which are nucleic acids) by organic dry weight, which is in good agreement with Anderson (1995), who reports a best estimate of 54.4% protein, 25.5% carbohydrate, and 20% lipid (0.8% of which are nucleic acids) for marine phytoplankton (Fig. 3). Using the H:C ratio of 1.65 after Anderson (1995) we calculate a mean composition of remineralized organic matter of $C_{123}H_{203}O_{65}N_{17}P$, which is in accord with the formula by Ríos et al. (1989) of $C_{129}H_{234}O_{70}N_{17}P$ for the elemental composition of phytoplankton. These results show that remineralization in the ocean indeed reflects the composition of the organic matter produced during primary production.

Summary—The estimation of reliable carbon Redfield ratios of remineralization has been complicated by the fact that anthropogenic CO_2 has penetrated the thermocline in most parts of the world ocean (and even deeper in the North Atlantic). Because the thermocline is also the depth regime where most of the biological remineralization signal is found, approaches to estimate Redfield carbon ratios from nutrient and oxygen data are, in most cases, subject to an anthropogenic bias. By correcting concentrations of dissolved inorganic carbon to preanthropogenic conditions, using reasonable estimates of the anthropogenic CO_2 content, we were able to remove this source of error. The corrections yielded tighter C_T -property correlations and caused significant changes in all carbon ratios.

Best estimates for Redfield ratios of remineralization are 1.34 ± 0.06 for $-O_2:C_{org}$ and 123 ± 10 for $C_{org}:P$. The $C_{org}:N$ ratio is regionally variable, with a mean value for the Northeast Atlantic Ocean (3–41°N) of 7.2 ± 0.8 . The $-O_2:P$ ratio of 165 ± 15 found here, excluding the shallowest isopycnal, confirms the generally accepted value of around 170 (e.g., Anderson and Sarmiento 1994). There is an indication of preferential remineralization of phosphorus in the upper thermocline. The best estimate for the N:P ratio of remineralization is 17.5 ± 2.0 . The elemental ratios obtained here are in good agreement with expected ratios based on the chemical composition of phytoplankton.

Although we were able to resolve differences in previously published Redfield ratios, some important aspects, such as regional and vertical variability, are beyond the scope of this study and need to be addressed further.

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References

- ANDERSON, L. A. 1995. On the hydrogen and oxygen content of marine phytoplankton. *Deep-Sea Res.* **42**: 1675–1680.
- , AND J. L. SARMIENTO. 1994. Redfield ratios of remineralization determined by nutrient data analysis. *Glob. Biogeochem. Cycles* **8**: 65–80.
- BREWER, P. G. 1978. Direct observation of the oceanic CO_2 increase. *Geophys. Res. Lett.* **5**: 997–1000.
- , C. GOYET, AND G. FRIEDRICH. 1997. Direct observation of the oceanic CO_2 increase revisited. *Proc. Natl. Acad. Sci. USA* **94**: 8308–8313.
- BROECKER, W. S. 1974. “NO”, a conservative water-mass tracer. *Earth Planet. Sci. Lett.* **23**: 100–107.
- , T. TAKAHASHI, AND T. TAKAHASHI. 1985. Sources and flow patterns of deep-ocean waters as deduced from potential temperature, salinity, and initial phosphate concentration. *J. Geophys. Res.* **90**: 6925–6939.
- CARPENTER, E. J., AND K. ROMANS. 1991. Major role of the cyanobacterium *Trichodesmium* in nutrient cycling in the North Atlantic Ocean. *Science* **254**: 1356–1358.
- , J. P. MONTOYA, J. BURNS, M. R. MULHOLLAND, A. SUBRAMANIAM, AND D. G. CAPONE. 1999. Extensive bloom of a N_2 -fixing diatom/cyanobacterial association in the tropical Atlantic Ocean. *Mar. Ecol. Prog. Ser.* **185**: 273–283.
- CASTRO, C. G., F. F. PÉREZ, S. E. HOLBY, AND A. F. RÍOS. 1998. Chemical characterisation and modelling of water masses in the northeast Atlantic. *Prog. Oceanogr.* **41**: 249–279.
- CHEN, C.-T. A. 1987. On the depth of anthropogenic CO_2 penetration in the Atlantic and Pacific Oceans. *Oceanol. Acta* **SP**: 97–102.
- , AND F. J. MILLERO. 1979. Gradual increase of oceanic CO_2 . *Nature* **277**: 205–206.
- , AND R. M. PYTKOWICZ. 1979. On the total CO_2 -titration alkalinity-oxygen system in the Pacific Ocean. *Nature* **281**: 362–365.
- COPIN-MONTEGUT, C., AND G. COPIN-MONTEGUT. 1983. Stoichiometry of carbon, nitrogen, and phosphorus in marine particulate matter. *Deep-Sea Res.* **30**: 31–46.
- EPPLEY, R. W., AND B. J. PETERSON. 1979. Particulate organic matter flux and planktonic new production in the deep ocean. *Nature* **282**: 677–680.
- GRUBER, N., J. L. SARMIENTO, AND T. F. STOCKER. 1996. An improved method for detecting anthropogenic CO_2 in the oceans. *Glob. Biogeochem. Cycles* **10**: 809–837.
- , AND ———. 1997. Global patterns of marine nitrogen fixation and denitrification. *Glob. Biogeochem. Cycles* **11**: 235–266.
- JOHNSON, K. M., A. KÖRTZINGER, L. MINTROP, J. C. DUINKER, AND D. W. R. WALLACE. 1999. Coulometric total carbon dioxide analysis for marine studies: measurement and internal consistency of underway surface TCO_2 concentrations. *Mar. Chem.* **67**: 123–144.
- JONES, E. P., AND E. M. LEVY. 1981. Oceanic CO_2 increase in Baffin Bay. *J. Mar. Res.* **39**: 405–416.
- KLEIN, B., AND M. TOMCZAK. 1994. Identification of diapycnal mixing through optimum multiparameter analysis. 2. Evidence for uni-

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- directional diapycnal mixing in the front between North and South Atlantic Central Water. *J. Geophys. Res.* **C99**: 25,175–25,280.
- KÖRTZINGER, A., L. MINTROP, AND J. C. DUINKER. 1998. On the penetration of anthropogenic CO₂ into the North Atlantic Ocean. *J. Geophys. Res.* **103**: 18,681–18,689.
- , W. KOEVE, P. KÄHLER, AND L. MINTROP. 2001. C:N ratios in the mixed layer during the productive season in the northeast Atlantic Ocean. *Deep-Sea Res. I* **48**: 661–688.
- MARTIN, J. H., G. A. KNAUER, D. M. KARL, AND W. W. BROENKOW. 1987. VERTEX: Carbon cycling in the northeast Pacific. *Deep-Sea Res.* **34**: 267–285.
- MCCARTNEY, M. S., AND L. D. TALLEY. 1982. The subpolar mode water of the North Atlantic Ocean. *J. Phys. Oceanogr.* **12**: 1169–1188.
- MILLERO, F. J., K. LEE, AND M. ROCHE. 1998. Distribution of alkalinity in the surface waters of the major oceans. *Mar. Chem.* **60**: 111–130.
- MINSTER, J.-F., AND M. BOULAHIDJ. 1987. Redfield ratios along isopycnal surfaces—a complementary study. *Deep-Sea Res.* **34**: 1981–2003.
- POLLARD, R. T., M. J. GRIFFITH, S. A. CUNNINGHAM, J. F. READ, F. F. PÉREZ, AND A. F. RÍOS. 1996. Vivaldi 1991—a study of the formation, circulation and ventilation of eastern North Atlantic Central Water. *Prog. Oceanogr.* **37**: 167–192.
- REDFIELD, A. C., B. H. KETCHUM, AND F. A. RICHARDS. 1963. The influence of organisms on the composition of sea water, p. 26–77. *In* M. N. Hill [ed.], *The Sea*. Interscience.
- 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. *Sci. Mar.* **53**: 779–784.
- SAMBROTTO, R. N., AND OTHERS. 1993. Elevated consumption of carbon relative to nitrogen in the surface ocean. *Nature* **363**: 248–250.
- SHAFFER, G., J. BENDTSEN, AND O. ULLOA. 1999. Fractionation during remineralization of organic matter in the ocean. *Deep-Sea Res. I* **46**: 185–204.
- SPEER, K. G. 1997. A note on average cross-isopycnal mixing in the North Atlantic Ocean. *Deep-Sea Res. I* **44**: 1981–1990.
- TAKAHASHI, T., W. S. BROECKER, AND S. LANGER. 1985. Redfield ratios based on chemical data from isopycnal surfaces. *J. Geophys. Res.* **90**: 6907–6924.
- TSUCHIYA, M., L. D. TALLEY, AND M. S. MCCARTNEY. 1992. An eastern Atlantic section from Iceland southward across the equator. *Deep-Sea Res.* **39**: 1885–1917.
- WANNINKHOF, R., S. C. DONEY, T.-H. PENG, J. L. BULLISTER, K. LEE, AND R. A. FEELY. 1999. Comparison of methods to determine the anthropogenic CO₂ invasion into the Atlantic Ocean. *Tellus* **51B**: 511–530.

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The influence of watershed land use on lake N:P in a predominantly agricultural landscape

Abstract—This study tests the hypothesis that lakes in watersheds dominated by row-crop agriculture (e.g., maize or soybeans) have systematically higher N:P than lakes in watersheds with large tracts of pasturelands. Current biogeochemical models of eutrophication suggest that agricultural nitrogen and phosphorus fluxes lead to a systematic decline in the N:P of receiving waters. In contrast, different agricultural activities (i.e., row-cropping vs. animal agriculture) use greatly divergent N and P amendments, and fluxes from agricultural watersheds diverge through a broad range of observed N:P (i.e., sub-Redfield to >100). Animal agriculture leads to low N:P fluxes and row-cropping to high N:P. The connection between agricultural watershed land use and lake nutrient stoichiometry was tested in a highly agricultural region of the United States (Iowa) on 113 lakes in watersheds with different amounts of row-crop (0%–95%) and pastureland (0%–36%). Multiple regression analysis shows that lakes in watersheds with large areas in pasturelands have low N:P, whereas lakes in watersheds dominated by row-cropping have systematically high N:P. Lakes in watersheds with >30% pasture had the lowest N:P, approaching Redfield levels. N:P was most frequently high (>50 as atoms) in lakes with >90% of their watersheds in row-crop agriculture. The dynamics of agricultural practice necessitates the inclusion of real-world differences among agricultural systems in nutrient stoichiometric models. Intensive row-crop agriculture yields N:P stoichiometry at high levels usually observed in pristine headwaters and open oceans, whereas increased animal agriculture will

drive N:P to low levels usually associated with cyanobacterial blooms.

Agricultural activities are a major source of nutrients to freshwater (Howarth 1996) and marine (Downing et al. 1999b) ecosystems. Nitrogen and phosphorus have been identified as leading pollutants in lakes, rivers, and estuaries (Carpenter et al. 1998). Agricultural nutrients (e.g., commercial fertilizer and animal manure) are rich in nitrogen and phosphorus and enter water bodies through surface and subsurface flow. Since nitrogen and phosphorus are the principal production-limiting nutrients in freshwater and marine systems, excessive loading of these nutrients can adversely affect receiving waters. The impacts of agricultural nutrients on freshwater and marine eutrophication worldwide are now well documented (Kronvang et al. 1993; U.S. Environmental Protection Agency 1995; Howarth et al. 1996; Downing et al. 1999a).

Both the quantity and stoichiometry of N and P influence aquatic primary production and community structure. Although N and P are essential to ecosystem function, the relative quantities (i.e., stoichiometry) of these elements are critical. When ambient nutrient supply ratios are extreme compared with biotic demand, ecosystem structure, function, and productivity are affected (Elser and Urabe 1999). In