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Redfield behavior of carbon, nitrogen, and phosphorus depletions in Antarctic surface water

Abstract—Inspired by the recent debate about anomalous nutrient utilization ratios in the surface oceans, we calculated depletions of total carbon dioxide, nitrate, and phosphate for the surface layer of the western Weddell Sea in summer. The depletion ratios, which incorporate all changes over a period of about 3 months starting from the onset of the vegetative season, essentially follow the classical Redfield model. We argue that reliable Redfield ratios can only be obtained when the time interval over which the nutrient utilization ratios are determined is comparable to the length of the vegetative season. Nutrient depletions are perfectly suitable to obtain reliable nutrient consumption ratios. We have good reason to believe that in the surface waters of the Antarctic, as they are nutrient replete, the nutrient consumption ratios comply with the classical Redfield values.

The oceanic biological pump is considered as the major pathway of biogenic element cycling. Part of primary production in the euphotic layer (new production; Dugdale and Goering 1967) is exported to deeper layers and to the seafloor via sinking of particles and downward mixing of dissolved organic matter. During its downward transport, organic material is remineralized and oxidized. Elemental cycling is ultimately completed such that CO₂ and nutrients are returned to the surface layer of the ocean through physical mixing and upwelling. The major part of the organic material produced in the surface layer, however, is recycled in situ. Changes in nitrate concentration in the surface layer predominantly reflect the removal by the photosynthesizing phytoplankton, whereas changes in phosphate and carbon dioxide are the net result of uptake and release processes. The consumption and production ratios of carbon, nitrogen, and phosphorus (C, N, and P, respectively) are indispensable properties, one of the most conspicuous applications being the scaling of nitrate removal by phytoplankton by a C:N ratio for obtaining the capacity of the biological carbon pump.

In their classical study, Redfield et al. (1963) proposed ratios of changes of dissolved C:N:P:O₂ of 106:16:1:–138 due to biological processes in oceanic thermocline waters; they also noted that this C:N:P:O₂ is about equal to the average composition of organic matter. Such ratios are now commonly known as Redfield ratios. In later investigations, these ratios for the thermocline and the deep ocean have been the subject of intense debate, either confirming or modifying the original Redfield ratios (Alvarez-Borrego et al. 1975; Takahashi et al. 1985; Minster and Boulahdid 1987; Peng and Broecker 1987; Fanning 1992; Anderson and Sar-

miento 1994; Shaffer 1996). Note that at depth, the dissolution of biogenic calcium carbonate contributes to changes of carbon, but this is corrected for by considering changes in the alkalinity. Takahashi et al. (1985) concluded that O₂:P ratios at depth in the Atlantic and Indian Oceans exceed Redfield values, also leading to higher C:P ratios. This was confirmed by Peng and Broecker (1987) but refuted by Minster and Boulahdid (1987), who suggested decreasing O₂:P ratios with depth. The most comprehensive analysis of all major oceans to date was conducted by Anderson and Sarmiento (1994). By accounting for mixing effects and applying neutral density surfaces, these authors in fact confirmed the original Redfield et al. (1963) stoichiometry, except for the nutrient to oxygen ratios. It should be noted that the work of Anderson and Sarmiento (1994) did not include the Southern Ocean because of insufficient data.

In the oceanic surface layer, Redfield ratios, the canonical or slightly modified ones, have often been used to derive the flux of one biological element from that of another. However, large-scale investigations addressing the ratios of nutrient variations have often excluded the oceanic surface layer. Recent studies by Laws (1991) and Sambrotto et al. (1993) have questioned the use of the classical C:N Redfield ratios in the surface layer. Laws (1991) used arguments related to the composition of organic material, which is apparently enriched in carbon with respect to nitrogen. Sambrotto et al. (1993) based their conclusions on dissolved carbon dioxide and nitrate time series data from different oceanic locations. They observed C:N ratios of 8.5–14, which significantly exceed the classical Redfield ratio of 6.6. If these high C:N ratios constitute the usual situation in the oceanic surface layer, translation of nitrate removal into carbon export by means of the Redfield ratio would systematically underestimate the capacity of the biological carbon pump.

Our aim is to investigate the C:N:P consumption ratios in the surface layer using austral summer data from the northwest Weddell Sea, which we determined from the ratios of the corresponding nutrient depletions. The latter represents the cumulative amount of nutrients removed from the surface layer during the ongoing productive period until the moment of sampling (Le Corre and Minas 1983; Jennings et al. 1984). The proportions of cumulative nutrient depletions render nutrient consumption ratios that are time-averaged over a longer period. Additionally, since nutrients are abundant in the Antarctic Ocean, their consumption ratios are not biased because of limitation of phytoplankton growth by lack of nutrients. Another reason for this investigation is that the “preformed” concentrations of properties in the

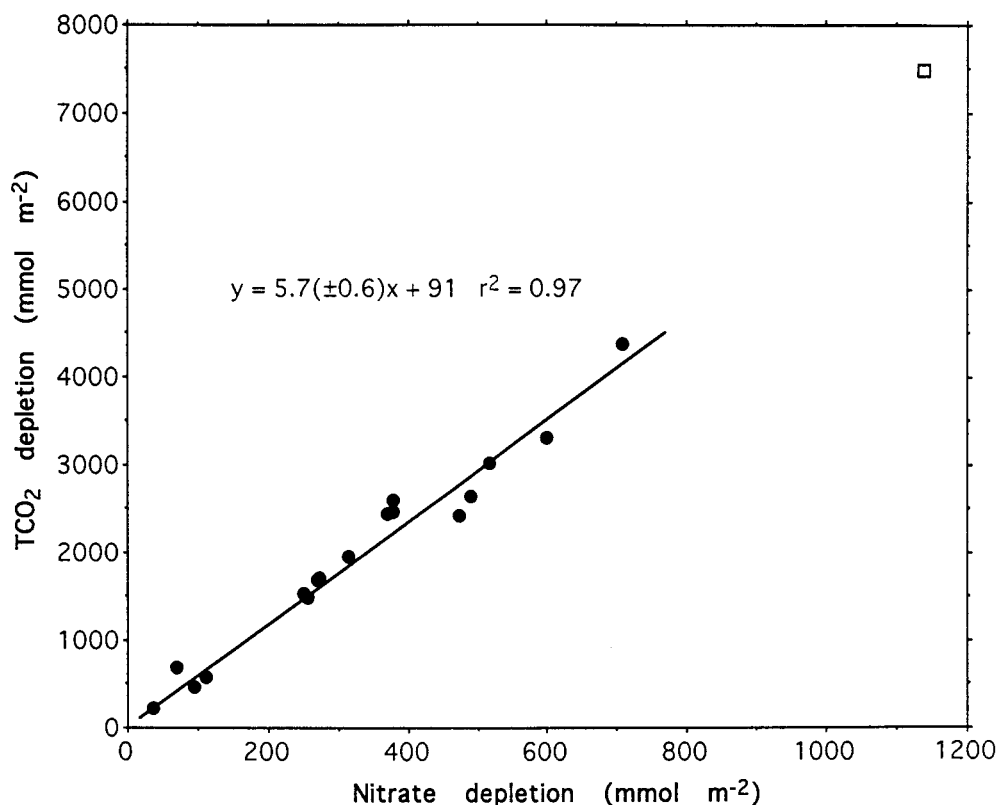


Fig. 1. Regression plot of TCO₂ vs. nitrate depletion for the surface layer in the western Weddell Sea in January 1993. One outlying data point (box symbol) was not considered in the regression. The relationship is significant. The slope of the regression line (with 95% confidence interval) yields the nutrient consumption ratio.

abyssal water masses in the oceans are mainly generated in the ice-covered part of the Antarctic Ocean. A thorough understanding of this area is therefore necessary.

Data collection.—TCO₂, nitrate, and phosphate data were collected on a cruise into the Weddell Sea aboard RV *Polarstern* in January 1993. The stations were situated on the continental shelf, slope, and rise on the eastern side of the Antarctic Peninsula between 63°S and 69°S. The TCO₂ concentration was determined with a precision of about 1 μmol kg⁻¹ using the coulometric technique (Stoll 1994). The concentrations of nitrate and phosphate were analyzed using an auto-analyzer system applying slightly modified standard colorimetric detection techniques (Kattner and Becker 1991). The precisions of nitrate and phosphate are 0.1 and 0.01 μmol kg⁻¹, respectively.

During spring and summer in the Southern Ocean, the upper part of the winter mixed layer warms up by heat input from the atmosphere, leading to a less dense surface layer, overlying a temperature minimum (near freezing point) just above the permanent pycnocline. The temperature minimum layer, located at 50- to 75-m depth, is a remnant of the winter mixed layer, thus serving as the perfect winter reference for the ensuing nutrient consumption through photosynthetic activity. The calculated depletions of total dissolved inorganic CO₂ (TCO₂), nitrate, and phosphate are integrated over the water column above the temperature minimum layer. They

constitute the resultant of all changes in nutrient concentration that have taken place since the formation of the summer surface layer, i.e., since the onset of the vegetative season.

Three assumptions are implicit in the calculation of nutrient depletions: (1) vertical homogeneity in the water underlying the ice cover is characteristic of late winter conditions, (2) vertical transport between the different layers and lateral transport are negligible, and (3) melting of nutrient-poor ice does not obscure the signal of nutrient changes. The latter effect was accounted for by normalizing the concentrations to a constant salinity. The transport processes are believed to have no significant influence on our results since the seasonal pycnocline between the summer surface layer and the temperature minimum layer effectively minimizes nutrient transport from below (Jennings et al. 1984; Goeyens et al. 1995; Hoppema et al. 1995). Moreover, as our results are obtained by constructing a regression of the depletions from several stations (*see next paragraph*), any possible influence of the processes just discussed is further diminished. The age of the summer surface layer by the time of sampling was about 3 months, as deduced from drifting buoys equipped with thermistor chains (Kottmeier unpubl. data).

Nutrient consumption ratios in the NW Weddell Sea—The ratios of the different nutrient depletions, derived from regression analyses on the station data (Figs. 1, 2), translate into 93 ± 23 : 15 ± 3 : 1 (±95% confidence interval) for the

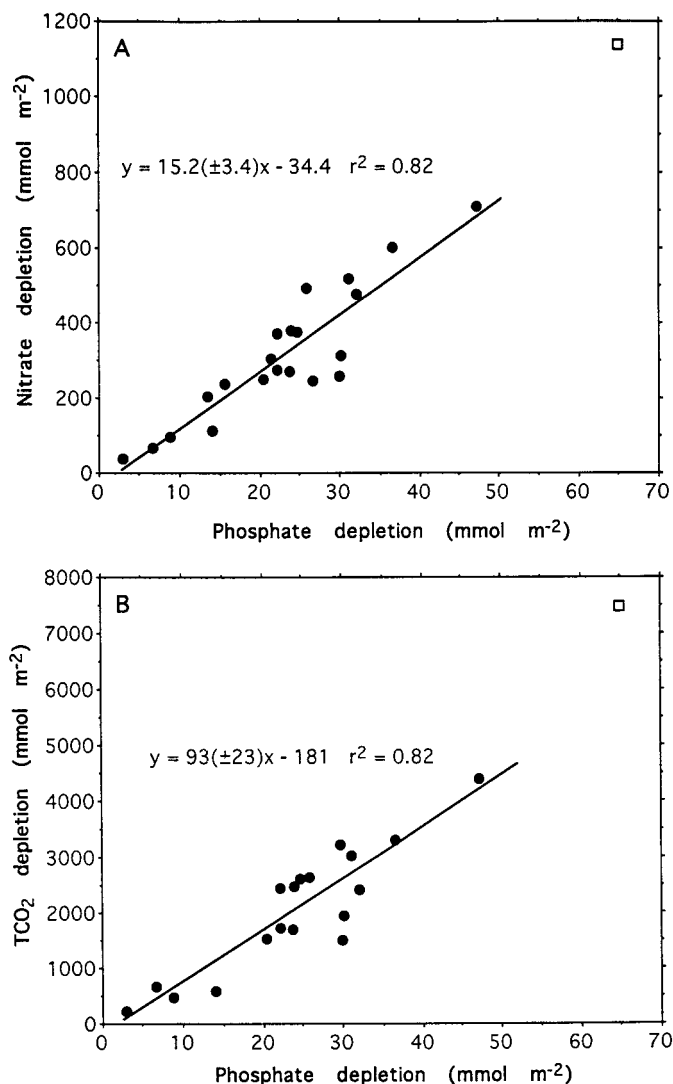


Fig. 2. Regression plots of (A) nitrate vs. phosphate depletion, and (B) TCO_2 vs. phosphate depletion for the surface layer in the western Weddell Sea in January 1993. One outlying data point (box symbol) was not considered in the regression. Both relationships are significant.

C:N:P values. It is evident that these relationships confirm the Redfield scheme of nutrient consumption (Redfield et al. 1963). One deviating data point from the continental shelf, showing much higher depletions than the rest, was omitted from the calculations (Figs. 1, 2) since it would skew the regression line out of proportion. The C:N ratio of 5.7 ± 0.6 (Fig. 1) is somewhat lower than the classical value of 6.6, but this difference is not statistically significant, the more so as the original Redfield et al. value has some error as well. Note that an average C:N ratio of 6.2 ± 1.1 is found when the TCO_2 depletion to nitrate depletion is calculated for all stations separately. The N:P ratio derived from regression is 15.2 ± 3.4 ($\pm 95\%$ confidence interval), whereas an all-station mean of 13.3 ± 3.1 is calculated.

Some comments on the part of TCO_2 are in order. Since CO_2 is a volatile species, TCO_2 concentrations in the summer

surface layer will be affected by photosynthesis as well as by air-sea exchange, a process that possibly biases the calculation of TCO_2 depletion. We assert that the invasion of atmospheric CO_2 only slightly influences the calculated TCO_2 to nutrient consumption ratios. This may be illustrated with the following calculation. Previously, Hoppema et al. (1995) estimated that the influence of atmospheric CO_2 on the surface layer up to January was equal to an increase of the TCO_2 concentration of the entire surface layer of $3 \mu\text{mol kg}^{-1}$. A fair estimation is that the maximal supply of atmospheric CO_2 during the ongoing season will not exceed $5 \mu\text{mol kg}^{-1}$. With a typical TCO_2 depletion of $3,000 \text{ mmol m}^{-2}$ (see Fig. 1) and a surface layer depth of 75 m, the TCO_2 depletion would be underestimated by about 10%, the corrected depletion being $3,375 \text{ mmol m}^{-2}$. This 10% difference is a relatively small, but non-negligible contribution. However, the TCO_2 to nutrient consumption ratios were calculated from a regression on several stations, the TCO_2 depletions of which all contain a contribution of atmospheric CO_2 . Therefore, we are confident that the underestimation of the TCO_2 depletion (and thus also of the C:N and C:P consumption ratios) is definitely smaller than the 10% tentatively calculated above.

Another potential interference for obtaining accurate TCO_2 to nutrient consumption ratios is related to the fact that biological activity does not only refer to soft tissue organic matter but also to biogenic calcium carbonate (e.g., shells). Processes involving calcareous material alter the TCO_2 content in the water but do not affect the other nutrients. Moreover, these alternative processes are not included in the Redfield model (Redfield et al. 1963). Whether or not calcium carbonate chemistry affects the TCO_2 concentration can be deduced from variations in the alkalinity. This potentially interfering effect is not significant in the Weddell Sea because the alkalinity is reported to be a conservative property; i.e., its variations are only due to changes in salinity (Poisson and Chen 1987; Anderson et al. 1991).

Our results corroborate the Redfield stoichiometry of nutrient consumptions in Southern Ocean surface waters but stand in sharp contrast with other studies. Sambrotto et al. (1993) emphasize the frequent occurrence of exceptionally high C:N ratios. They refer to Antarctic data from Karl et al. (1991), which seem to comply with the trend of high C:N ratios. However, in our view, the C:N removal ratio calculated by Karl et al. (1991) is deceptive. Upon inspection of the diagram from which this anomalously high C:N ratio was derived (see fig. 9A in Karl et al. 1991), it appears that the slope is strongly forced by a few points with low nitrate and TCO_2 concentrations. If these few odd data points are omitted from the regression, the obtained ratio amounts to 5.4 ± 1.0 ($r = 0.7$). This is substantially lower than the reported value of 10.4 ± 0.7 ($r = 0.9$), and it is in fair agreement with the Redfield value. Other anomalous nutrient consumption ratios for Antarctic waters, reported by Jennings et al. (1984) and Whitehouse et al. (1995), refer to low N:P ratios (< 15). In contrast, Le Jehan and Tréguer (1983) observed essentially Redfield-like behavior of nitrate to phosphate depletions.

The time factor—In our view, the crucial factor in interpreting all these different results is the length of the time interval over which the nutrient consumption is considered. Banse (1994) already addressed the considerable variability in uptake ratios observed during short-term mesocosm studies, thus pointing out the significance of the time factor. In all previous studies that found non-Redfieldian nutrient consumption ratios, the typical time span considered was about 1 month or less. Both our study and that by Le Jehan and Tréguer (1983) refer to longer time periods of about 3 months and reveal Redfield behavior of nutrient depletions. Implicitly, the observational time period is crucial for the nutrient consumption ratios since nutrient removal shows ample seasonal variability, depending on the actually dominant biological process. Both nutrient removal (uptake by phytoplankton) and supply (regeneration by heterotrophic activity) processes are affected by short-term variability in plankton community structure and functioning and, hence, in the amount and composition of organic matter that is either recycled in the euphotic layer or sequestered below the pycnocline (Banse 1994; Roman et al. 1995; Rivkin et al. 1996). Such expressions of food-web control and the concomitant seasonal progression from predominantly autotrophic to heterotrophic structures affect the particulate elementary ratios as well as the nutrient consumption ratios. External factors such as temperature and irradiance (e.g., Brzezinski 1985) or minor nutrient stress (De Baar et al. 1997) can additionally cause significant variation of the nutrient consumption ratios. In any case, the overall nutrient depletion ratios exhibit short-term variability. Earlier investigations already noticed marked variability on both a spatial and a temporal scale (Banse 1974; Goldman et al. 1979; Laws 1991). All of this strongly underpins the importance of timing of the observations during the season. An illustration of this can also be found in Sambrotto et al. (1993), who observed different C:N ratios during two different periods in spring on the same location. Obviously, when the observational time interval is ≤ 1 month, variable nutrient ratios can be found. In our data, an equivalent of this effect is discernible. If we would only consider the depletion data from a particular subregion, e.g., the continental shelf, we would find different nutrient consumption ratios. Only because a wide range of depletion values is used (Figs. 1, 2), corresponding to a relatively long period of photosynthetic activity, the calculated nutrient consumption ratios appear to align with the classical Redfield model. The observational time period for our data is about 3 months, which at high latitudes in Antarctic regions covers a large part of the vegetative season. Under such circumstances, Redfieldian nutrient utilization ratios appear to be prevalent in the Antarctic surface layer.

Conclusions—The classical Redfield et al. (1963) model holds for the surface waters of the Weddell Sea (this study) and probably also for other sectors of the Southern Ocean. For other oceanic regions, the situation may be more complicated. In most studies that report larger deviations from the classical Redfield ratios, the observational time period has been relatively short. Thus, the deviating nutrient consumption ratios may be an expression of short-term vari-

ability of biological systems in the upper oceans. In contrast, a substantial contribution of molecular nitrogen fixation by cyanobacteria, as observed by Karl et al. (1997) in the subtropical Pacific Ocean, would cause a shift to nitrogen-supported new and export production, which results in enhanced N:P removal ratios both in particulate and dissolved matter. Although the literature on phytoplankton compositions in the Southern Ocean is quite extensive, we are unaware of major occurrences of nitrogen-fixing organisms south of the Polar Front. Similar deviations from the Redfield value of nutrient removal ratios are therefore not to be expected in Antarctic waters. The basic requirement for obtaining acceptable Redfield ratios for surface waters remains that the vegetative season must be largely covered by the sampling period. In this regard, it should be realized that Redfield ratios calculated for the deep oceans inherently refer to time scales of many years. Reliable results in the surface layer are obtained by calculating Redfield ratios from nutrient depletions.

The acquisition of Redfield ratios from particulate organic matter production may be prone to considerable bias because the particles exhibit patchy distributions as well as highly variable compositions. Moreover, recent work has provided strong support for the view that dissolved organic material is at least as important for the export of organic matter out of the euphotic zone as the particulate organic fraction (Toggweiler 1989; Carlson et al. 1994; Lefèvre et al. 1996). This argument adds to our view that the correct way to obtain Redfield ratios is from differences in dissolved nutrient concentrations, which incorporate all changes be it through particulate or dissolved organic matter production.

The corollary to our finding that Redfield stoichiometry is valid in the upper Weddell Sea is that no discrepancy exists between nutrient utilization in the upper ocean and nutrient release in the deep ocean. This conclusion is not in contradiction with redistribution mechanisms resulting in accumulation of organic species enriched in a particular element in the surface layer (e.g., Williams 1995) or with other fractionating effects, if these occur only seasonally. At the same time, this implies that net nitrate consumption in the Southern Ocean can be used as a means to approximate net community carbon production and carbon export from the surface layer.

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