New production and the $f$ ratio around the Crozet Plateau in austral summer 2004–2005 diagnosed from seasonal changes in inorganic nutrient levels

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Abstract

Recent mesoscale iron-fertilisation experiments suggest that iron may be an important micronutrient in HNLC regions but estimates of carbon export from such experiments are inconclusive. An alternative strategy to estimate export from such environments is to observe naturally productive ecosystems associated with topography. One such system is the Crozet islands and associated plateau (Crozet), at 46°S, 52°E. Each year a large bloom of phytoplankton occurs to the north of Crozet with a reduced bloom occurring to the south. We use nitrate data from the Crozet region collected during austral summer 2004–2005 to estimate new production (NP) via the Redfield ratio. Peak integrated values of up to 50 g C m$^{-2}$ to the north of the plateau and up to 15 g C m$^{-2}$ to the south are inferred. We estimate total integrated primary production (TP) using satellite techniques and calculate $f$ for each station. Overall NP is linearly related to TP. However, $f$ declines at very high levels of TP because nitrate usage ceases despite continuing PP and because nitrate levels increased from their postbloom low. This results either from a resupply of nitrate from beneath the thermocline due to mixing processes or to the mixed-layer ammonification and nitrification of accumulated organic nitrogen. We discount the first possibility because our estimates of the mixing flux of nitrate appear to be inadequate to cause the entire recovery in nitrate levels, and because any mixing flux of nitrate would likely be accompanied by a resupply of iron, which would induce NP to occur and erode the resupply of nitrate. Instead we consider the recycling of accumulated organic nitrogen to be a more likely explanation based on our observation of high organic nitrogen levels in the mixed layer north of Crozet during the cruise. The implications of this conclusion are that euphotic zone nitrification is a significant process, and that in this system new and export production are not equivalent. This recycling is sufficiently large that it reduces our estimate of NP north of the plateau to a level where it is equivalent to NP in the south. Whether a similar refertilisation of the mixed layer occurred in the south of the study region, which would be consistent with a meridional gradient in carbon export, is unknown due to the limited duration of the shipboard programme.

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1. Introduction

The transfer of carbon from the atmosphere to the ocean is facilitated in part by the uptake of dissolved inorganic carbon by phytoplankton in the euphotic zone and the subsequent removal of this material from the surface waters; a process known as the biological pump (Eppley and Peterson, 1979) which transports approximately 10 GT Carbon yr\(^{-1}\) beneath the seasonal thermocline (Prentice et al., 2001). The biological pump is strong in the high-latitude North Atlantic and coastal upwelling regions, and weak in subtropical gyres and in the Southern Ocean (SO) (Falkowski et al., 1998). These low values in the SO, which occur despite high levels of macronutrients, likely result from the low levels of plant biomass, have led to it being termed one of the high nutrient–low chlorophyll (HNLC) regions.

Mesoscale experiments suggest that the HNLC status of the SO may result from a deficiency of iron (de Baar et al., 2005) but estimates of the role of iron in regulating export in the SO from such experiments have been hard to obtain (de Baar et al., 2005; Buesseler et al., 2004). Observations of carbon export from naturally productive regions such as the marginal ice edge and the Polar Front suggest significant export in regions such as the Ross Sea and the Polar front at 170\(^\circ\)W (Buesseler et al., 2001, 2003). An alternative strategy is to observe naturally productive ecosystems associated with small islands as they likely result from topographic iron release (Blain et al., 2001; Bucciarelli et al., 2001; Korb and Whitehouse, 2004; Holeton et al., 2005; Planquette et al., 2007).

One such system is associated with the Crozet islands, (46\(^{\circ}\)S, 52\(^{\circ}\)E) at the northern margin of the SO in the Polar frontal zone (Fig. 1). Here the Subantarctic Front (SAF), the most northerly front of the eastward flowing Antarctic Circumpolar Current (ACC), is deflected north due to topography immediately west of the Crozet plateau/island complex (Crozet) before retroreflecting eastwards at a latitude of 42\(^{\circ}\)S. South of this latitude, but north of Crozet itself exists a region with weak mean circulation occupied by water derived from the HNLC SO. This has moved northwards by a combination of Ekman drift and the northwards movement of a minor fraction of the SAF, which becomes detached from the major branch of the SAF at 48\(^{\circ}\)S, 48\(^{\circ}\)E and moves east south of Crozet before turning north at a longitude of 52\(^{\circ}\)E (Pollard et al., 2007).

A large bloom of phytoplankton occurs regularly each year in the region between 42\(^{\circ}\)S and 46\(^{\circ}\)S (Pollard et al., 2002) with its western and northern sides constrained by the northwards and eastwards flowing SAF. The water in which this bloom occurs has experienced considerable interactions with the topography of Crozet during its passage north, leading to an iron stimulation of production (Pollard et al., 2007; Venables et al., 2007; Planquette et al., 2007). Iron enrichment incubation experiments in the Crozet basin conducted by Sedwick et al. (2002) suggests significant iron-limitation of plankton growth in the open-ocean sectors associated with the SAF.

**RRS Discovery** made a diverse range of observations North and South of Crozet between early November 2004 and mid-January 2005. This paper reports observations of nitrate concentrations and uses them to estimate new production in the study region to test the hypothesis that the intense plankton bloom is accompanied by substantial nitrate utilisation, and hence that new production levels and the potential for carbon export are also high as one would expect, based on Eppley and Peterson (1979) and Laws et al. (2000), as discussed below.

The method employed involves observing the depth-integrated seasonal decrease in nutrient concentrations over the course of an annual cycle. This strategy has been employed in Antarctic waters by Jennings et al. (1984) and Green and Sambrotto...
(2006) and in the North Atlantic by Garside and Garside (1993) and Campbell and Aarup (1992) using data from Glover and Brewer (1988). A complication is that some fraction of the nitrate utilised during new production is converted to dissolved organic nitrogen which accumulates in surface seawater over the course of the productive season before mineralisation in winter (Anderson and Williams, 1999) and to particulate organic nitrogen which is not necessarily exported. If any accumulated organic nitrogen is recycled to nitrate prior to winter overturning then this accumulation represents production which is new but not exported.

Estimates of seasonal changes in nitrate levels only allow us to derive estimates of new production. In the absence of an independent estimate of primary production over the same time period as that covered by the estimate of new production derived from nitrate utilisation, it is impossible to determine how new production scales to total production, i.e. the magnitude of the $f$ ratio. Early work proposed a simple relationship between new and total production (Eppley and Peterson, 1979), whereas more recent work (Laws et al., 2000) proposes a temperature-related algorithm. Understanding the details of this relationship is important as it will allow new production to be computed with a similar resolution as the high-resolution maps of primary production routinely created from sea-surface chlorophyll images.

To address this problem, we therefore compare nitrate removal integrated over the course of the productive season to total production estimated over the same period. Our estimates of integrated primary productivity are based on satellite remote sensing, because the shipboard sampling programme commenced in the period following the peak chlorophyll $a$ concentrations in the north of the study area. This allowed an $f$ ratio to be derived for each station, which integrates all processes occurring in the period prior to the occupation of that station.

Hence the relationship between $f$ and total production can be derived, which should allow superior estimates of new production to be made in similar waters simply from chlorophyll imagery, and the evolution of the $f$ ratio as the bloom proceeds can be examined. This study complements those of Seeyave et al. (2007) and Lucas et al. (2007) who report observations of $^{234}$Th disequilibria and POC:Th ratios and use them to estimate carbon export and Venables et al. (2007) who report details of the validation of satellite chlorophyll $a$ data.

2. Methods

2.1. Cruise track and sampling strategy

Nitrate samples were taken from CTD casts from early November 2004 to mid-January 2005 in the waters around the Crozet Islands (Fig. 1, Table 1). At a subset of these stations (designated M stations in Fig. 1; see Seeyave et al., 2007) instantaneous column-integrated primary production was measured using the $^{14}$C technique and simulated in situ techniques on samples collected from a titanium rosette sampler using trace clean techniques. Dissolved oxygen (DO) was measured on samples collected from the stainless steel rosette.

2.2. Inorganic nutrients

Samples were drawn directly from Niskin bottles into polystyrene coulter counter vials and stored at 4 °C until analysis, which commenced within 12 h of sampling. Nitrate + nitrite (hereafter nitrate) was determined using a Skalar Sanplus autoanalyser following Sanders and Jickells (2000). Overall, the precision of the data is estimated to be ±0.5 μmol L$^{-1}$ (2.5% of the top standard). Consistency of the data was ensured by the analysis of commercial nutrient standards (Ocean Scientific International, Petersfield, Hants, UK) at regular intervals on each cruise and by the comparison of deepwater nutrient concentrations between stations. Concentrations of nitrate determined in the commercially available nutrient standards were within 5% of their designated values.

2.3. Dissolved oxygen

DO was measured on all bottles from each CTD cast using a semi-automated whole-bottle Winkler titration unit with spectrophotometric end point detection manufactured by SIS <www.sis-germany.com>. Samples were drawn directly from the Niskin bottles into 100-ml volume-calibrated oxygen bottles, their temperature measured, and DO fixed immediately using alkaline iodide and manganous chloride solutions prepared following Dickson
Table 1
Values of primary and new production and of $f$ calculated following methods described in the main text

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<th>Days since bloom began</th>
<th>Nitrates removal to date (mmol m$^{-2}$)</th>
<th>New production to date (g C m$^{-2}$)</th>
<th>Minimum peak rate of New C prodn (g C m$^{-2}$ day$^{-1}$)</th>
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<td>C</td>
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Each station is described by a date, latitude and by a Discovery station number; some stations are also designated an M number corresponding to a specific process station from the cruise. Most stations are also designated N (North), C (Central) or S (South) depending on whether new production calculated at them has been compared to time integrated from the N, C or S box shown in Fig. 1. Also shown are estimates of the peak daily rate of new production derived by normalising integrated nitrate removal scaled by the Redfield ratio to an estimate of the number of days elapsed since the bloom began (September 1 in N and C regions and November 1 in S region).
(1994). The thiosulphate solution was regularly standardised using a commercially available 0.01 N potassium iodate standard (Ocean Sciences International). Concentrations and percentage saturations were calculated following Dickson (1994). A minimum of one bottle of each cast was sampled twice to gain an estimate of the analytical precision. The mean difference in calculated oxygen concentration between all the duplicate pairs sampled was <1%.

2.4. In situ primary production and chlorophyll

Primary production was measured using the $^{14}$C technique at six depths in the euphotic zone (Seeyave et al., 2007). Chlorophyll was determined fluorometrically following Welschmeyer (1994). See Seeyave et al. (2007) for further details.

2.5. New production calculations

We assume (an assumption justified below) that nitrate concentrations; at 100 m represent winter concentrations; these are then extrapolated to the surface and both the extrapolated and observed profiles integrated to 100 m. The difference between the two integrals is then calculated to determine nitrate removal in units of mmol m$^{-2}$ (column 8 of Table 1) and converted to moles of carbon (column 9 of Table 1) using a Redfield ratio of C = 6.6 N (Redfield et al., 1963) following Hoppema et al. (2002). Clearly the choice of Redfield ratio used can significantly influence the calculated carbon export.

For example, Rubin et al. (1998) found a C/N utilisation ratio of 6.9±0.6 in the Pacific sector of the SO and concluded that the biological cycles of carbon and nitrogen in the SO are ‘Redfieldian’. Sweeney et al. (2000) found elevated removal ratios (7.8 for diatom dominated waters and 7.2 for Phaeocystis dominated waters) in the Ross Sea. Li and Peng (2002) found a ratio of 5.3 in the SO from an analysis of nutrients and DIC. Brzezinski et al. (2003) found a gross uptake ratio of 5.2 and a net uptake ratio of 9.1 in the Pacific sector of the SO between the Antarctic Polar Front (APF) and the ice edge. Rubin (2003) found a net uptake ratio of 6.63 south of the Polar Front in the Pacific sector and 6.6 north of the Polar Front. Bozec et al. (2005) found a net uptake ratio during Eisenex of 5.9. Thus there appears to be no consensus on how Redfield ratios vary in the C/P ratio than in the C/N ratio (Rubin, 2003) and that taxonomic variability, particularly south of the Polar Front plays a significant role. In the absence of any consensus, we therefore use the canonical value of 6.6 and justify this on the basis of in situ observations from this campaign. Integrated C/N uptake ratios from the major bloom event sampled were 6.6±1.5 and integrated particulate ratios from the same event were 6.2±0.5. (Lucas et al., 2007). However, it is important to recognise that the conversion to carbon units carries with it some uncertainty in the estimate of new production derived from changes in nutrient concentrations. For this reason we return in Section 4.2 to expressing estimates of NP in nitrogen units.

Allowances are also made in Section 4.2 for new production generated from nutrient additions to the system, which may not be reflected in the seasonal drawdown, using data on atmospheric N inputs presented in full in Planquette et al. (2007) and the diffusive flux of nitrate from deeper waters based on observations of mixing rates presented by Charette et al. (2007).

2.6. Justification of integration depth

Venables et al. (2007) suggest that the depth of winter mixing and hence the likely depth of the winter nutricline across the study region is of the order of 200 m; however, it is preferable to integrate to a shallower depth if possible, to ensure that only processes occurring within the upper euphotic zone are included in the analysis. The deepest summer mixed layers in the region are of the order of 100-m (Venables et al., 2007) and this provides a powerful reason for integrating to this depth since we wish to include all processes occurring in the upper ocean on a seasonal basis as a consequence of euphotic zone planktonic activity. This depth choice is now confirmed to be reasonable based on the distribution of nitrate and oxygen in the region. Using the value at 100 m to represent winter concentrations makes an implicit assumption that the upper ocean is completely mixed in winter. In the south of the study area, where minimal nutrient removal had occurred prior to the initial observations, little vertical variation in the upper 100 m was observed, supporting a 100-m integration. However, elsewhere, it is clear that some vertical structure, which is inferred to be caused by removal rather than by incomplete mixing, is present. To test whether this inference is valid DO levels are now considered
following Koeve (2001), who argues that surface winter nutrient levels are those which occur in waters with 100% oxygen saturation.

Fig. 2A shows DO data analysed in a similar manner to that of Koeve (2001). Some variability is seen in the oxygen data. Shallower than 100 m oxygen saturation is generally in excess of 100% (18% of data points have saturations < 100%) due to net photosynthesis, whilst below this depth saturation is generally less than 100% (11% of data points have saturations greater than 100%) due to the export and respiration of organic matter. At approximately 100 m oxygen saturations are 100% saturated (mean value = 98 ± 3.3%), implying according to Koeve (2001) that nitrate concentrations at this depth are representative of those found in winter at that site. Regression analysis using a model II regression yields a relationship of nitrate

e = -0.55 \times \text{oxygen saturation} + 78.6, \quad r^2 = 0.6, \quad p > 0.001

between the nitrate and O_2 saturation data. This suggests that nitrate concentrations in unmodified (O_2 saturation = 100%) winter water are likely to be 23.6 μmol L\(^{-1}\).

The mean value of nitrate observed at 100 m was 24 ± 1.8 μmol L\(^{-1}\) (Fig. 3). However, between 90 and 110 m 21 of 35 oxygen samples were undersaturated and 14 were supersaturated. Hence, in some of the waters at 100 m some oxygen respiration had occurred, and hence will have had nitrate levels in excess of winter values (conversely, some will have had nitrate removed from them in new production). Referencing the calculation of nitrate removal to this depth thus introduces some uncertainty into the calculated level of new production. However, conducting integrations to a deeper depth where all the oxygen saturations were <100% or to a

Fig. 2. (A) Dissolved oxygen saturation (%) plotted against depth in metres for all stations shown in Fig. 1 (B). Regression between nitrate and dissolved oxygen saturation for stations shown in Fig. 1. The regression shown is a model II regression, which minimises the residuals between observed and modelled data perpendicular to each data point.
shallower depth where all were >100% would introduce a systematic bias, rather than the random one, resulting from using 100 m as a common level across all stations. Fig. 3 also suggests that below 100 m nitrate levels are homogeneous laterally across the study area (no significant correlation between nitrate and latitude exists at 100, 150 or 200 m, whereas clear depletions are seen north of the plateau in both the 10 and 50 m datasets), thus using the value at 100 m as a ‘winter’ value appears reasonable. Nitrate concentrations at 100, 150 and 200 m show some mesoscale variability as expected from the results of Pollard et al. (2006), who showed that only beneath 350 m are nutrient concentrations in the SO laterally homogeneous. This variability should not affect our estimates of NP since nutrient deficit calculations at each station are referenced to a 100-m value from that station, and hence any mesoscale variability in deep nutrient concentration is inherently accounted for in our deficit calculations. The alternative possibility, of using a single ‘winter nitrate’ value for every station is clearly unwise.

2.7. $f$ Ratio calculations

Each station was classified as being either north of the plateau (N), in the centre of the study region (C) or south of the plateau (S). (Table 1). The time evolution of chlorophyll $a$ concentrations in these regions was then determined using data from boxes located in the N, C or S of the study region as follows. Daily and 8-day 9-km-level 3 mapped SEAWIFS/MODIS merged products were downloaded from $<$http://oceancolor.gsfc.nasa.gov$>$. These were then validated by comparing shipboard chlorophyll measurements to the value from the corresponding pixel in the merged images. A total of 224 such matchups were possible, yielding a regression of $\text{Chl}_{\text{merged}} = 0.12 + 0.38 \times \text{chlorophyll}_{\text{in situ}}, \ r^2 = 0.78, \ p<0.001$. For further details see Venables et al. (2007). From these validated composite images time series of chlorophyll $a$ in the three boxes identified in Fig. 1 were then compiled, starting from August 4, 2004.

Seeyave et al. (2007) show a strong relationship between surface chlorophyll and column integrated production in the study region ($\text{in situ}$ primary production in $\text{mg C m}^{-2} \text{d}^{-1} = 462 \times \text{surface chlorophyll} a$ in $\text{mg Chl m}^{-3} + 110, \ r^2 = 0.97, \ n = 19, \ p>0.001$). This is used to estimate production for each week in the three regions shown in Fig. 1. To allow a direct comparison between the productivity values and the new production values estimated as described above, which represented integrated nitrate utilisation over the productive season up to the date of sampling, satellite-based estimates of primary production for each week calculated as described above are integrated up to each sampling date from August 4 in all study areas. In performing these calculations missing chlorophyll data points were linearly interpolated. An $f$ ratio was then

![Fig. 3. Nitrate concentrations in µmol$^{-1}$ at nominal depths of 0, 50, 100, 150 and 200 m plotted from all stations shown in Fig. 1.](http://oceancolor.gsfc.nasa.gov)
calculated by comparing integrated primary production obtained from satellite techniques as described above and integrated new production from nutrient deficits at each site. The f ratios derived here are values averaged over time and not instantaneous ones such as those derived by Lucas et al. (2007) from 15N uptake experiments.

Overall the mixed-layer information presented by Venables et al. (2007), the latitudinal distribution of nitrate shown in Fig. 3 and the DO data shown in Figs. 2A and B all support the concept of estimating seasonal new production by evaluating nutrient deficits in the upper 100 m relative to winter stocks calculated by assuming the value at 100 m to be representative of winter conditions.

3. Results

3.1. Spatial distribution of nitrate concentrations

Fig. 3 shows nitrate concentrations at a range of depths plotted against latitude. A clear reduction in surface nitrate concentration is seen in the region north of Crozet (18 μM) relative to the region south of Crozet (24 μM). This strong gradient is replicated at 50 m; however, at 100, 150 and 200 m the distributions of nitrate do not have any clear meridional gradient. This is the first suggestion that surface waters to the north of Crozet have reduced nitrate concentrations, consistent with elevated levels of new production in this region.

3.2. Chlorophyll concentrations

Venables et al. (2007) present a detailed analysis of the time evolution of the bloom in the study region based on satellite imagery. Fig. 4 shows the time series of mean chlorophyll a concentration in three regions within the study area. Firstly, in the north of the region, secondly, in the centre of the region and thirdly, to the south (Fig. 1), with error bars representing the range of all data points within the box.

To the north of Crozet, chlorophyll concentrations peak at about 4 mg m\(^{-3}\), in the central region, at about 2 mg m\(^{-3}\) and south of Crozet, at about 0.7 mg m\(^{-3}\). The bloom peaked at the end of October in both the N and C regions (prior to the earliest shipboard observations made there and 2.5 months before the latest shipboard observations from those regions). It peaked in mid-December in the southern region (after the earliest shipboard observations in that region and approximately 2 weeks earlier than the latest shipboard observations in that region).

This large-scale gradient in bloom magnitude is consistent with a release of iron from the plateau and fertilisation of the northern and eastern regions as detailed by Planquette et al. (2007). The later
peak in production south of the plateau is consistent with regional differences in heating and stratification, which are believed to control the local variation in bloom timing (Venables et al., 2007).

3.3. Estimates of primary and new production

Using the methods described above time-integrated primary production from satellite remote sensing, time-integrated new production from nutrient deficits and the $f$ ratio have been calculated at each of the 54 stations within the study area (columns 6, 9, 11, respectively, of Table 1). Values of time-integrated primary production from satellite techniques range from 28 to 114 g C m$^{-2}$, of new production from 0 to 60 g C m$^{-2}$ and of the $f$ ratio from 0 to 0.7. Also shown are nitrate deficits at each station in mmol m$^{-2}$ (column 8 of Table 1), an estimate of the number of days since the bloom began in each region (column 7 of Table 1, taking September 1 as the first day of the bloom in the northern and central regions and November 1 as the first day of the bloom in the southern region) and an estimate of the minimum peak rate of new production in g C which must have occurred (column 10 of Table 1).

4. Discussion

This study has two objectives. The first is to test the hypothesis that new production is higher to the north of the plateau than to the south, consistent with iron fertilisation of the waters to the north. The second is to test the hypothesis that the ratio of new to total production (the $f$ ratio) is related to the magnitude of primary production. Before addressing these two hypotheses the estimates of nitrate removal made here are compared with similar estimates from the region around South Georgia and Kerguelen and to other regions within the SO. Additional sources of nutrients, which may have augmented the production calculated from the seasonal removal of nutrients, are then evaluated.

4.1. Comparison with nitrate removal from other Subantarctic island systems and the wider Southern ocean

The waters to the north of Crozet show a clear reduction in nitrate concentration, consistent with an iron stimulated export of organic carbon. A maximum reduction of about 8 $\mu$M is observed, which is about 72% of the maximum removal of nitrate observed in the region NW of South Georgia (ca. 11 $\mu$M; Whitehouse et al., 1996), a region where iron stimulated nitrate removal is believed to be significant (Korb and Whitehouse, 2004). The reduction around Crozet is substantially larger than the nitrate removal around Kerguelen shown by Blain et al. (2001) in regions where turbidity is believed to be an important factor (3 $\mu$M, Fig. 4 of Blain et al., 2001).

Thus overall the Crozet system appears to be slightly less productive than the South Georgia region, a factor which may be accounted for by the smaller landmass of the Crozet Archipelago relative to the island of South Georgia. However, this conclusion is based on only one season of data around Crozet and interannual variability in the region may be large enough to discount this conclusion. We now compare the drawdown estimates made here with similar estimates made in the open SO. Green and Sambrotto (2006) estimate an average removal of 0.27 mol N m$^{-2}$ from north of the APF to the South Antarctic Circumpolar Front. This is approximately half of the maximal removal seen around the Crozet System (Table 1) and hence suggests that the NP induced by the island system is significantly larger than that which occurs naturally in the open ocean sectors of the SO.

4.2. Inputs of nutrients through mixing and atmospheric deposition

Small-scale diapycnal mixing is likely to mix some nutrients across the thermocline. This can be calculated by the product of the mixing rate and the gradient of nutrients at 100 m, which is, at maximum, 0.02 mmols m$^{-4}$. Values for the vertical mixing rate around Crozet have been derived by Charett et al. (2007) in 2 ways. Firstly, the distribution of the naturally conservative tracer radium has been analysed to obtain an estimate of 11 cm$^2$ s$^{-1}$ and secondly, LADCP data has been analysed to give an estimate of 0.35 cm$^2$ s$^{-1}$. Application of these two mixing rates to the gradient above over a 100-day productive season gives values of nitrate flux into the photic zone capable of sustaining 16.5 and 0.48 g C m$^{-2}$ new production, respectively, over the course of the study.

Planquette et al. (2007) suggest that the dry atmospheric deposition of nitrogen is of the order of 2 nmol m$^{-2}$ d$^{-1}$, which over a 100-day productive
season could support a new production level of 0.016 g C m\(^{-2}\). Clearly the mixing supply of new nitrogen has the potential to significantly enhance the estimates of new production made above, by up to 16.5 g C m\(^{-2}\), whereas the atmospheric source is much less important. There are insufficient data to fully characterise the spatial variability in the mixing flux; however, it is likely to be largest in the north of the study area, where nitrate gradients are steepest due to the higher depletions observed there. The mixing flux is therefore, not included in the subsequent discussion. However, the likely gradient in the mixing flux will amplify the strong N/S gradient in diagnosed new production documented in Fig. 5A.

4.3. Spatial variability in new production

Fig. 5A shows integrated new production to the date of sampling plotted against latitude. Clearly values are higher to the north of the plateau with values of 25–57 g C m\(^{-2}\) occurring to the north of 46°S and values of 0–15 g C m\(^{-2}\) to the south of 46°S. Thus the initial hypothesis that new production is higher to the north of Crozet is consistent with an enrichment of HNLC waters, which have interacted with shallow topography during northwards motion, enrichment of HNLC waters, which have interacted higher to the north of Crozet is consistent with an enrichment of HNLC waters, which have interacted with shallow topography during northwards motion, appears valid. Lucas et al. (2007) have independently derived estimates of integrated nitrate utilisation by combining the time series of chlorophyll \(a\) in the three regions with the Seeyave et al. (2007) regression of sea-surface chlorophyll to instantaneous primary production and an empirical regression of the \(f\) ratio determined using \(^{15}\)N techniques to surface chlorophyll \(a\). They find similar levels of integrated new production in each region (North = 32.3 g C m\(^{-2}\), Central = 17.9 g C m\(^{-2}\), South = 5 g C m\(^{-2}\)), supporting the calculations presented here. They also estimate the level of iron enrichment of the water column required to support the estimates of integrated new production they present and the timing of iron depletion in each region.

The levels of iron enrichment required are consistent with the independently obtained estimates of maximal winter iron levels calculated by Planquette et al. (2007), based on radium and iron gradients away from the islands and the area of the plateau. The timing of iron removal is calculated to be such that most of the removal would have occurred associated with the peak in chlorophyll \(a\) levels that occurred prior to our earliest shipboard observations. Thus, despite the fact that Planquette et al. (2007) report that the northern region had, at the time of our observations, only slightly higher iron levels in the southern region, with surface values of the order of 0.1–0.2 nM, it appears plausible that the enhanced chlorophyll and nitrate removal (Figs. 3 and 4) seen north of Crozet is caused by iron enrichment.

Considerable variability is apparent in calculated new production in the northern and central regions, where multiple stations were occupied over the 2-month period of the cruise. This scatter is not removed by normalising the integrated nitrate removal to the number of days which had elapsed since the bloom began to create a daily rate of new production (Table 1, daily rates up to 0.79 g C m\(^{-2}\) day\(^{-1}\)), although the same general pattern is observed. Conceivably this implies large variability in the rate of new production at stations close to each other in the high chlorophyll area over periods of several weeks. However, this suggestion should be treated with caution, since some days or weeks within this period will have had low levels of new production (when the bloom had not yet matured), whilst others will have had high levels of new production (when intense plankton growth had occurred). They must, therefore, be treated as lower limits of the peak daily rates that must have occurred.

Undertaking this calculation is nevertheless a useful exercise as the new production rates it implies can be compared with independently derived estimates of export to determine their validity. These rates are larger than the \(^{234}\)Th based export estimates made by Morris et al. (2007) who suggest values of up to 0.35 g C m\(^{-2}\) day\(^{-1}\) in the northern region. They are also larger than the fluxes estimated by Salter et al. (2007), who suggest fluxes at 100 m of up to 0.4 g C m\(^{-2}\) day\(^{-1}\) based on the results from drifting neutrally buoyant sediment traps. This implies either that in the system studied levels of new and export production are not equal, i.e. that not all new production is exported, or that the method described here overestimates new production. This issue is discussed further below.

4.4. Relationship between time integrated new and primary production

Fig. 5B shows the relationship between new production and primary production, both integrated to the date of sampling. There is a clear tendency for new production diagnosed from nitrate
Fig. 5. (A) Plot of accumulated new production derived from mixed-layer nitrate deficits against latitude, (B) plot of accumulated new production from mixed-layer nitrate deficits against total time-integrated primary production determined from satellite chlorophyll \( a \) concentrations using the regression between column-integrated primary production and surface chlorophyll \( a \) concentration given by Sweeney et al. (2007) and (C) plot of \( f \) ratio (integrated new production/total time integrated primary production) against total time-integrated primary production. Regression in panel B is for all datapoints. Points labelled MS derive from a targeted survey of a mesoscale eddy towards the end of the programme, which may not be representative of the region they are from. Boxes N, C and S enclose data points from stations in the north, central and southern areas, respectively (Fig. 1).
removal to increase as time integrated primary production increases. Model II regression analysis of the relationship between new and primary production yields oceanographically inconsistent results with a predicted level of new production at zero primary production levels of \(-15\text{ g C}\). We therefore describe the relationship between these parameters using a model I regression. This yields a relationship of 

\[ \text{New Production} = 0.29 \times \text{Primary production} \]

\( (r^2 = 0.49, P > 0.001) \) implying a mean \( f \) ratio of 0.29 for the region as a whole. Note that the linearity of this relationship is unexpected as \( f \) is expected to increase as primary production does. This point is now addressed via a regional analysis.

It is noticeable that the data on Fig. 5B cluster into three groups. Points at production values of \(<45\text{ g C m}^{-2}\) are derived from the southern region, between 45 and 75 \(\text{g C m}^{-2}\) from the central region and greater than 80 \(\text{g C m}^{-2}\) from the northern region. This segregation appears hard to rationalise since the populations in the northern and central regions must have had periods when they had only fixed an integrated amount of carbon below the peak level calculated in the southern region. The segregation results from the blooms at the two northern locations being different in magnitude, with inferred different levels of time-integrated primary production, and our only having sampled the northern and central regions once most of the primary production which took place in these regions had occurred. The southern region has low values of integrated total time because the peak level of chlorophyll \(a\) in this region was lower than the peak values in the north and central regions, and because we commenced our sampling prior to the peak value of chlorophyll \(a\) achieved in the south of the study region.

In the southern and central regions there is a tendency for new production to increase with increasing production. This is logical since new production is expected to be linked positively to primary production (Laws et al., 2000; Eppley and Peterson, 1979). In the central region this conclusion is biased by the three highest export datapoints (denoted MS), which are derived from a deliberate targeted survey of a mesoscale bloom close to the islands. However, even if these three points are ignored, the conclusion that time integrated new primary production are positively correlated in these regions is robust.

However, in the northern region as time integrated primary production increases, new production appears to decrease (Fig. 5B). It is important not to overstate this tentative conclusion as, whilst there is a large cluster of data at production levels of about \(90\text{ g C m}^{-2}\), only three datapoints suggest a reduction occurred (two at 90 and one at \(115\text{ g C m}^{-2}\) and the range in new production calculated at time-integrated primary production levels of \(100\text{ g C m}^{-2}\) is large. This inferred reduction in new production occurs because nitrate deficits calculated towards the end of the sampling period declined relative to those calculated in the early part of the observation period. This issue is revisited later when reasons exploring the general overestimate in new production from nutrient drawdown relative to thorium deficits and drifting traps are discussed.

4.5. Relationship between \(f\) ratio and time-integrated primary production

Fig. 5C shows the relationship between the \(f\) ratio and time-integrated primary production. The mean value of the individual values of \(f\) calculated across the entire dataset is 0.24, similar to the value of 0.29 derived from the regression analysis of Fig. 5B described earlier in Section 4.4. Again, three clusters of data are seen, one corresponding to each of the regions shown in Fig. 1. Each of these clusters shows a similar pattern to that observed for the analogous cluster in Fig. 5B. The southern region shows an increase in \(f\) ratio towards a value of 0.3 by, the central region values of 0–0.25 (neglecting the mesoscale bloom stations), and the northern area suggests a decline in \(f\) with time. In addition to the reduction in nitrate deficits discussed earlier, which by themselves would cause a reduction in estimated \(f\) ratio, this is because time integrated primary production in this region continued to increase over the course of the cruise, albeit at low rates, with no accompanying reduction in integrated nitrate levels.

The values of the \(f\) ratio seen in Fig. 5C appear reasonable in the context of other direct observations of the \(f\) ratio in the SO. For example, Mengesha et al. (1998) found \(f\) ratios ranging between 0.39 and 0.69 in the Indian sector of the SO with low values corresponding to summer observations and the high values to the spring bloom. Similarly Goeyens et al. (1998) found values of 0.39 to 0.86 and Bode et al. (2002) found values of 0.39 and 0.42 in open ocean situations in the Bellingshausen Sea and Gerlache strait, and a value
of 0.64 in a plankton bloom in the western Bransfield strait.

4.6. Time evolution of new production

Fig. 6 shows time series of new production, displayed as the mixed layer nitrate deficit rather than in carbon units as in Fig. 5C to eliminate uncertainties associated with the conversion to carbon units from uncertainties in the appropriate Redfield ratio to use discussed earlier, in the three regions shown in Fig. 1. As suggested by Figs. 5B and C, the magnitude and timing of nitrate removal varied in the three regions.

4.6.1. Southern region

To the south new production was modest, reaching values of 200 mmol N m$^{-2}$ in the period after the peak in chlorophyll $a$ levels in this region.

4.6.2. Central region

In the central region nitrate removal persisted for some days after the peak in chlorophyll $a$ concentration that occurred at the beginning of November, until at least December 23–24. It is tempting to conclude from Fig. 6 that new production continued until January 10 in this region; however, the three datapoints which lead one to this conclusion are from the mesoscale feature and the cluster of datapoints at the same time with levels of nitrate removal export of 200 mmol N m$^{-2}$ may be more representative of the mean situation at this time. If this safer analysis is accepted, then new production likely peaked around late December or earlier, around 1 month after the bloom in the region has reached its maximum chlorophyll $a$ level (Fig. 4).

4.6.3. Northern region

In the northern region levels of new production were highest immediately on arrival in the study area (500–700 mmol N m$^{-2}$), consistent with the larger bloom observed in the vicinity (Fig. 4). They then declined to levels of 300–500 mmol N m$^{-2}$ by late November and appear to have declined further thereafter to values of 200 mmol N m$^{-2}$ in late December. Levels of new production cannot have actually declined, assuming that we consider new production to be production supported by nitrate, since the nitrate has been used and removed from the upper ocean, either via sinking or via a storage as organic matter. If the latter term is important then it implies that the estimate of NP made in the early part of the study from nutrient deficits are over estimates of the potentially exportable production.
The suggestion of declining levels of new production over time calculated from the nitrate deficit data is caused by an increase in nitrate levels in the euphotic zone in the northern region. What processes might be causing this refertilisation of the mixed layer? Mesoscale or diapycnal mixing processes are obvious candidates; we can set an upper limit over their importance using the earlier calculation that they could support up to 16.5 g C m\(^{-2}\) (equivalent to 180 mmol N m\(^{-2}\)) in a 100-day period. The nitrate deficit in the upper ocean declined by about 400 mmol m\(^{-2}\) (Fig. 6), suggesting that, at most, such processes could be responsible for about 50% of the refertilisation observed. Even a contribution of this magnitude is unlikely as mixing processes would probably mix up some dissolved iron and thereby allow further assimilation of nitrate to proceed. On this basis it seems unlikely that vertical mixing is responsible for the refertilisation of the mixed layer by nitrate. The alternative candidate is the ammonification and nitrification of dissolved and/or particulate organic nitrogen synthesised during the initial plankton bloom that has not been exported.

Levels of particulate organic nitrogen in the upper water column of 2–3 \(\mu\)mol L\(^{-1}\) were frequently observed in the north of the study region towards the end of the shipboard programme, 2 months after the peak in chlorophyll \(a\) observed at that latitude (Sanders et al., unpublished). Further the seasonal accumulation of dissolved organic nitrogen in the Irminger Basin, a comparable high-latitude system, was of the order of 30–40% of nitrate removed over similar timescales (Sanders et al., 2005). These points both add support to this suggestion. In addition Morris et al. (2007) suggest on the basis of \(^{234}\)Th-depletion data that a much weaker meridional gradient in carbon export than in either primary or new production occurred in the study area. A storage of organic matter in the upper ocean in the post bloom phase over a period of several months, as suggested by the distribution of nitrate deficits presented in Fig. 6, would be consistent with this hypothesis.

Overall the estimate of new production in the north of the study region by the end of the observation period is only slightly higher than the estimate of new production in the south of the study region at the same time. Thus, despite the fact that peak levels of new production in the north were substantially larger than the values diagnosed in the south of the study region a refertilisation of the mixed layer by nitrate, likely by the recycling of organic nitrogen within it, reduced the meridional gradient in calculated new production substantially by the end of the shipboard programme. Whether a similar refertilisation of the waters in the south of the study region occurred following the shipboard study is impossible to say.

5. Conclusions

Fig. 4 shows clearly that significantly increased levels of integrated primary production occur in the region north of the Crozet islands compared with the HNLC region to the south. In the post bloom period this gradient in integrated primary production induced higher levels of new production in the region north of the Crozet plateau than in the region to the south. However, sustained observations of the region north of the plateau (Fig. 6) suggest that a gradual refertilisation of the mixed layer by nitrate, likely due to the ammonification and nitrification of organic nitrogen, occurred and hence that not all of this fixed organic nitrogen was exported. The implication of this conclusion is that euphotic zone nitrification is an important process in the study area, and that in this system new and export production are not equivalent. Whether a similar refertilisation of the mixed layer with nitrate occurred south of the plateau during the shipboard sampling programme is unknown.

References


Morris, P., Sanders, R., Thomalla, S., Tarnawitsch, R., 2007. $^{254}$Th derived particulate organic carbon export compared to new production from an island induced phytoplankton bloom in the Southern Ocean.


