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Nutrients in an oligotrophic boundary current: Evidence of a new role for the Leeuwin Current

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Running Head: Leeuwin Current and nutrient sources

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Nutrients in an oligotrophic boundary current: Evidence of a new role

for the Leeuwin Current.

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30 Abstract

New observations along the continental shelf of Western Australia provide a novel explanation for the established ~60 y relationship between Leeuwin Current (LC) strength and greater winter nitrate concentrations at 32°S plus the interannual variation in the magnitude of the annual, shelf-scale, phytoplankton bloom. The potential source of dissolved nitrogen to support the

- 35 annual shelf scale phytoplankton bloom was identified as thin layers of an unprecedented areal extent, nitrate concentration and shallow nature that were observed off the northwest of Australia. We propose that the dissolved inorganic nitrogen (DIN) in these layers enters the LC at depth and then enters the euphotic zone via by three mechanisms: instability that results in a warm core eddy, cooling that deepens the surface mixed layer and shallowing of the thin layer. During the onset of the
- 40 annual phytoplankton bloom along the west coast of Australia from 22°S to 34°S the poleward flowing LC was clearly evident as a surface intensified ocean boundary current transporting warmer, lower-salinity, greater-silicate waters in a shallow mixed layer rapidly southward. Between 24 and 26°S the core of the LC was present as a 50 to 100 m deep layer over one or more thin layers, 15 to 50m thick, with high nitrate and low dissolved oxygen (DO). These layers were of lower salinity,
 45 cooler water with markedly reduced DO, high nitrate concentrations and distinct nitrate:silicate (NO₃:Si(OH)₄) nutrient ratios. As the LC flowed south it cooled and deepened thereby entraining the thin layers of high nitrate water into the euphotic zone. The LC also formed large (greater than 100km diameter) warm core eddies with a deep surface mixed layer that also entrained nitrate from
- 50 of high nitrate intact but now within the euphotic zone. Thus, the available evidence suggests the LC arises under conditions that favour rapid and shallow nitrification. This nitrification fuels a shelf scale bloom on a downwelling favourable coast. Depending upon the rate of nitrification the source of the particular organic matter may be local or delivered from the tropics via horizontal advection in a subsurface layer of the LC.

these thin layers. In some locations as far south as 32°S the LC was still present with the thin layer

55 Key words: nutrients; phytoplankton bloom; Australia; nitrification; eddy; vertical mixing; thin

layers. Accepted

Introduction

- The central gyre of the Indian Ocean from 5 to 45°S is amongst the world's most oligotrophic regions with a very low standing stock of phytoplankton (Polovina et al. 2008). Previous phytoplankton ecologists have indeed described the eastern Indian Ocean as a desert (Wood 1964). The region of the eastern Indian Ocean along the west coast of Australia experiences a midwinter peak in phytoplankton biomass (a bloom in the desert) that spans more than 15° of latitude and extends from the coast to several hundred km offshore (Moore et al. 2007). The source
- of nutrients to support this bloom has been the subject of considerable debate with several hypotheses being advanced (Feng et al. 2009) including transport (Koslow et al. 2008) in the Leeuwin Current (¹LC), a coastal source (Dietz et al. 2009), upwelling (Hanson et al. 2005), deep mixing associated with eddy formation (Waite et al. 2007), or seasonal cooling that results in deepening of the seasonal thermocline and the entrainment of more nitrate into the euphotic zone
- 70 (Koslow et al. 2008). The magnitude of the annual west coast bloom is known to vary in proportion to the strength of the Southern Oscillation Index (Thompson et al. 2009) as does the strength of the Leeuwin Current (Feng et al. 2003); both are greater during La Niña events. These spatial and temporal patterns of variations in nutrients and phytoplankton suggest that the strengthening LC somehow delivers more nutrients into the euphotic zone.
- 75 The Leeuwin Current arises due to geostrophic transport from the Indonesian Throughflow that generates an alongshore steric height gradient, sufficient to overcome the equatorward wind stress and suppress the Ekman driven upwelling, thus limiting the supply of nutrients to the surface waters (Pearce, 1991). Off the west coast of Australia the buoyant Leeuwin Current (LC) flows strongly poleward at the surface along the shelf break, peaking at 7 Sv in midwinter (Feng et al.

¹ Abbreviations: Leeuwin Current (LC), low dissolved oxygen and high nitrate (LDOHN), dissolved inorganic nitrogen (DIN), particulate organic matter (POM), organic matter (OM), warm core (WC), cold core (CC), . diadinoxanthin (DD), diatoxanthin (DT), fluorescence (Fl).

80 2003) and covering much of the region with a thin layer of warm, relatively fresh water. Relative to the surrounding waters the LC carries greater concentrations of silicate and phosphate but concentrations of dissolved inorganic nitrogen (DIN) remain low through winter (Johannes et al. 1994, Lourey et al. 2006) suggesting that the growth of phytoplankton in these shelf waters is limited by the availability of N.

85 Previous evidence for upwelling along the west coast of Australia is restricted to one location and one time of the year. In the SW corner of the continent during the summer period, when the Leeuwin Current is nearly nonexistent, strong northward winds can drive a cold Capes Current from the Capes Leeuwin and Naturaliste region (Pearce and Pattiaratchi, 1999). Localized Ekman-driven upwelling of cold deep water associated with the Capes Current is hypothesized as the basis of some

90 localized increase in primary production (Gersbach et al. 1999, Hanson et al. 2005). There is little evidence for upwelling along other regions of the west Australian coast although it has been suggested as a possible mechanism responsible for the sporadically high rates of primary production observed at ~ 25°S (Hanson et al. 2005).

At mid latitudes (~ 32°S) increased phytoplankton biomass and primary production were observed in deeply mixed warm core eddies (Thompson et al. 2007). The source of nitrogen to support these productive warm cores eddies was hypothesized to be entrainment from coastal waters (Greenwood et al. 2007, Dietz et al. 2009) or eddy induced upwelling (Waite et al. 2007). Previous studies of mesoscale variation off the west coast of Australia identified newly forming eddies to contain more nitrate in the euphotic zone (Paterson et al. 2008) and for mature eddies to contain

100 greater phytoplankton biomass (Moore et al. 2007). Some component of the inter-annual variability in regional productivity must be associated with the greater mesoscale eddy energy during La Niña years (Fang and Morrow 2003, Feng et al. 2005) as a single WC eddy represents an increase of ~6000 tons in particulate organic carbon (Feng et al. 2007). The winter shelf (Thompson and Waite 2003) and eddy microplankton (Thompson et al. 2007) tend to be diatom dominated, a characteristic

105 often associated with relatively deep mixing, low average irradiances and nitrate as the nitrogen source (Lomas and Glibert 1999, 2000, Litchman and Klausmeier 2001, Litchman et al. 2004).

ACCEPTED MANUSCRIPT At most locations around the world the average winter nitrate concentration is negatively

correlated with sea surface temperature (e.g. Switzer et al. 2003, Kamykowski and Zentara 1985), but this is not true for west Australian shelf waters where warmer winter temperatures are associated

- 110 with greater surface nitrate concentrations (Thompson et al. 2009). In most of the world's oceans convective cooling and increased wind during winter acts to deepen the seasonal thermocline and resupply the euphotic zone with nutrients including nitrate (Kamykowski and Zentara 1985). Off most of west Australia, however, the annual amplitude in the depth of the mixed layer reported to be only 10 m (Condie and Dunn 2006) which is a remarkably small seasonal deepening of the seasonal thermocline relative to these latitudes on the east coast of Australia (Condie and Dunn 2006) or the
- 100 m found in some regions of the ocean (Sprintall and Roemmich 1999). This small amplitude in mixed layer depth (MLD) may be associated with the winter flow of the buoyant LC.

In this study we undertook a shelf scale survey off Western Australia during the period when Leeuwin Current flow was increasing and the annual primary production cycle was nearing its peak

120 (May-June). In our search for the nutrient source to support this bloom we increased the spatial resolution of sampling relative to any previous research along this coast. Bottle samples for nutrient analysis were obtained at relatively narrow depth increments (≥10m). Ultraviolet spectrophotometric detection of nitrate concentrations (Johnston and Coletti 2002) were undertaken as a component of most CTD casts giving ~ 1 estimate of nitrate concentration m⁻¹. Cross-shelf sections of temperature, salinity, fluorescence, dissolved oxygen and transmission were collected via a towed, undulating CTD system. The nutrient concentrations in the euphotic zone (0 – 100m) were examined and regions of greater concentrations investigated in detail for potential sources and mechanisms of injection. Potential links between surface mixed layer nitrate concentrations and vertical mixing were investigated by considering the degree of stratification and evidence that the surface mixed layer was actively mixing.

Based upon the results a description of the processes that deliver dissolved inorganic nitrogen into the euphotic zone along the continental shelf off western Australia was developed (Fig. 1). The results indicate the presence of a shallow layer of low dissolved oxygen and high nitrate water

offshore and just below the high phytoplankton biomass found in the surface mixed layer of the LC

- 135 between 22 to 25°S (Fig. 1). This layer is transported south along the base of the LC (Woo and Pattiaratchi 2008). Southwards and near the Abrolhos Islands the Leeuwin Current narrows developing high eddy kinetic energy (Feng et al. 2005). South of the Abrolhos Islands the LC produced a large warm core eddy observed off the shelf at ~ 31°S with relatively high nitrate and low dissolved oxygen plus N:Si ratios. These characteristics are indicative of the nitrate in the eddy
- 140 resulting from entrainment of the layer from the base of the LC. The LC cools as it progresses southwards and further south, off Perth (~32°S), the LC existed in 2 modes. One mode with nitrate from this thin layer mixed throughout the surface mixed layer (purple colour) and another with the thin layer still intact but at relatively shallow depths (~ 70m).

MAT

145 Materials and Methods

Physics

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Onshore – offshore transects were conducted along each degree of latitude from 34°S to 22°S along the west coast of Australia. In general CTD profiles were obtained at water depths of 25, 50, 75, 100, 200, 300, 500, 750, 1000, and 2000 m on each transect, with at least one station positioned to be in the middle of the LC. A total of 111 stations were vertically profiled during the cruise using a Seabird SBE 911 instrument (CTD) to measure conductivity (converted to practical salinity units), pressure (converted to depth [m]) and temperature (°C). Most vertical profiles also contained photosynthetically active radiation (PAR, 400 to 700 nm, Biospherical Instruments QCP-2300), fluorescence (Chelsea Instruments AquatrackaTM fluorometer), % transmission (Wetlabs C–StarTM),

155 dissolved oxygen (Anderra 3975 series optode) and nitrate (Satlanic ISUS sensor) concentrations.

The Seabird 911 conductivity sensor was validated against 184 bottle samples analysed for salinity and showed a small standard deviation of 0.002 PSU. These data were then averaged over 2m depth increments. Mixed layer depth was calculated using temperature and salinity (after Condie and Dunn 2006) as the depth at which the temperature was 0.4°C less than that observed at 10m or salinity was 0.03 more than that measured at 10m. At each CTD station the mixed layer depth was the shallower of these two. From each CTD profile the gradients in temperature, salinity, dissolved oxygen, fluorescence and percent transmission were calculated from 0 to 50m, 50 to 100m and 100 to 150m. These gradients between different parameters were examined for associations (Pearson correlations) that might reflect consistency in vertical structure between parameters. They were also assessed for association with nitrate in the euphotic zone.

A towed undulating body (Seasoar) was used to provide high resolution sections across the Leeuwin Current. A typical undulation was ~ 150m requiring about 6 minutes and over a single transect across the LC provided hundreds of vertical profiles for temperature, salinity, dissolved oxygen, fluorescence and % transmission. The majority of transects between the inshore station at

- one latitude and the offshore start of another set of CTD stations along the next fixed latitude were surveyed by Seasoar, for example, the 150 km transect between the inshore station at 34°S (114.9°E) and the offshore station at 33°S (113.8°E). Continuous underway data recorded on the vessel, RV *Southern Surveyor*, included surface PAR, wind speed, direction, surface temperature, salinity, fluorescence, bottom depth and ADCP measured current velocities from a vessel mounted RDI 70
- 175 kHz Ocean Surveyor Acoustic Doppler Current Profiler (ADCP) (Teledyne RD Instruments). The instrument was set to record from just below the ship (~ 10m) to a maximum water column depth of 300 m and data were averaged in 8 m depth bins.

Chemistry

- Bottle samples (n ~ 851) from multiple depths (range 0 to 1949m) from 111 CTD casts were analyzed for nitrate, nitrite, ammonium, silicate and phosphate concentrations using Quick-ChemTM methods on a flow injection LACHAT® instrument as per the following protocols for nitrate + nitrite (Quik-ChemTM Method 31-107-04-1-A; detection limit ~0.03 µM; adapted from Wood et al. 1967), silicon (Quik-ChemTM Method 31-114-27-1-D; detection limit ~0.05 µM; adapted from
- Murphy and Riley 1962) and phosphate (Quik-ChemTM Method 31-115-01-1-G; detection limit ~0.02 μM; adapted from Armstrong 1951). Samples were analyzed for ammonium on the LACHAT® instrument using the technique of Kerouel and Aminot (1997) adapted for flow injection, detection limit ~ 0.05 μM. The Satlantic ISUSTM sensor was included on CTD profiles < 1000m. Up-cast nitrate profiles derived from in-situ ultraviolet spectrometry (IN) were calibrated
- against bottle samples (BN) [BN = 1.22IN 0.29; r² = 0.92], and were corrected for temperature dependent hysteresis (Johnson and Coletti 2002) and individual cast offsets likely associated with thermal shock and/or false blank (dark voltage) on deployment.

Dissolved oxygen (DO) concentrations from 162 bottle samples were measured by automated Winkler titration on a Metrohm 765 DosimatTM. These were compared with the Aanderra model

195 3975 optode fitted to the CTD system. In general the optode showed good agreement with the chemically determined concentrations (Fig. 2A). In particular the optode sensor did not

underestimate chemically measured DO. A few chemical measurements were lower than those estimated by the sensor and these were not used in the calibrating the sensor. This early model optode had quite slow response times and possibly due to the thin layers of low DO water

- 200 (sometimes less than 10m thick) there may not have been sufficient time for equilibrium at the vertical velocity 1 m s⁻¹ normally used during a CTD profile. In some regions narrow layers of low dissolved oxygen were at relatively shallow depths and most often below a strong pycnocline. In these regions the observed concentration of dissolved oxygen was compared with the solubility of oxygen for the prevailing conditions of temperature and salinity after Garcia and Gordon (1992).
- 205 The solubility concentration (DO*) minus the observed concentration = subsaturation. For the purpose of assessing the respiration represented by this subsaturation as a potential source of nitrogen the organic matter (OM) was assumed to have 1:1 and 6.6:1 ratios for O:C and O:N, respectively (Fraga et al. 1998) and the apparent oxygen utilization (AOU = theoretical 0₂ solubility observed O₂ concentration) was calculated from the classic "Redfield model" (Redfield, 1942).
- Over the depth range of 0 100 meters the agreement between observed nitrate (bottle samples) and potential nitrate concentrations estimated from the respiration of OM by this method was reasonable $(r^2 = 0.48)$, especially at concentrations greater than 0.3 µM nitrate (Fig. 2B). The slope of $1.71\pm$ 0.08 (P < 0.001) suggests at least 60% of the potential N remineralized over these depths was present in the water column as nitrate.

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Biology

A variable number of stations was sampled for biological parameters in a manner designed to give approximately consistent cover of three regions at each degree of latitude. The regions were defined as inshore of the Leeuwin Current (~ 50m deep), in the centre of the Leeuwin Current (~ 200 to 300m deep) and offshore (1000 or 2000m deep). Fifty four stations and 6 depths (n = 520) from 0 to < 300 m were sampled and 2 size fractions (greater than 0.7 µm, collected on Whatman GF/FTM filters and greater than 5 µm, collected on 5µm NitexTM mesh) were extracted in 90% acetone over-

night at -20°C and analysed for chl*a* on a calibrated Turner Designs model 10 AU fluorometer (Parsons et al. 1984).

- Two size fractions (less than 5 m and greater than 5 micron) were collected from three stations per latitude and 2 depths per station for analysed by HPLC to determine a suite of pigments using Waters® instrumentation (a Waters 996 Photodiode Array Detector, a Waters 600 Controller, and a Waters 717plus Autosampler). The HPLC system used an SGE 250 x 4.6 mm SS Exsil ODS (octodecyl silica) 5 µm column. Pigments were eluted over a 30 minute period with a flow rate of 1
- 230 ml min⁻¹. The Van Heukelem and Thomas (2001) method was used which gave improved resolution to chlorophylls c₁ and c₂, and full resolution of MV and DV chlorophylls a and b, lutein and zeaxanthin. Each solvent was pre-filtered through a Millipore HVLP 0.45 µm filter. The separated pigments were detected at 436 nm and identified against standard spectra using EmpowerTM software. Concentrations of the pigments were determined from standards (Sigma® and purified
- 235 pigments obtained from algal cultures).

Rates of vertical mixing.

Typically wind stress or surface cooling are the major forces that increase mixing, weaken stratification and can increase the vertical transfer of nutrients into the euphotic zone. As pointed out
by Huisman et al. (1999), however, even with vertical gradients in physical parameters that are small enough for a layer to be defined as mixed, the rate of vertical mixing can be so slow that chemical and biological gradients develop. Therefore the vertical gradients were assessed using temperature, salinity, DO, chla fluorescence and phytoplankton pigments. The latter approach uses the physiological adjustment of phytoplankton to light as a very sensitive method to assess rapid vertical mixing. Cells rapidly adjust their cell quota of photoprotective pigments in response to variation in irradiance, or depth, and these pigments can be used to estimate how long cells have been away from the surface. Normalizing to chla improves the precision of the estimate (Claustre et al. 1994, Moline 1998). The intracellular concentration of the photoprotective pigments diadinoxanthin (DD) and diatoxanthin (DT) photoacclimate on a time scale of minutes to hours (Brunet et al. 2003). If the rate

of vertical mixing is relatively rapid then the observed difference (DD+DT)/chla over a change in depth (Δz) will be small relative to changes observed in a more stable water column. The vertical displacement velocity in the euphotic zone can be calculated from:

$$\frac{\Delta z}{\Delta t} = \frac{\Delta z(-k)}{\ln[(R_t - R_{\infty})/(R_0 - R_{\infty})]}$$
 eqn. 3.

where k is the first-order rate constant for the photoacclimation parameter of choice, R_t is the

255 parameter at time t, R_0 is the same parameter at time zero, R_∞ is the parameter after an infinite time of photoacclimation, and Δz is the vertical distance between the surface and the depth of 1% surface irradiance (after Falkowski 1983). For the purpose of calculating mixing rates the lowest observed value of (DD+DT):MVchla was selected as R_∞ . A k value of 0.5 h⁻¹ was adopted from the literature (Claustre et al. 1994, Moline 1998, Brunet et al. 2003).

MA

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Results

Background and study area

The cruise commenced on May 15th 2007 just prior to the onset of austral winter and, as anticipated, we sampled as the regional phytoplankton bloom approached its annual maximum (Fig 3, inset C).

- 265 Relative to climatology, the phytoplankton bloom in 2007 in the study region (111 to 116°E and 35 to 21°S) was 30% less than normal (1997-2010). Shipboard ADCP showed considerable current velocities (~ 1 m s⁻¹) along the entire coast, mostly in the southward direction, but strong northwards flow were observed in some locations (Fig. 3B). Remotely sensed estimates of sea surface height and sea surface temperature showed the LC flowing southward at this time and the presence of
- 270 anticyclonic (warm core) eddies at ~23, 28, 31 and 34°S (Fig. 3A). Daily updates from remote sensing were used to aid navigation during the research voyage including the facilitation of a complete east-to-west transect through the large warm core eddy between 31 and 32°S.

General overview of nutrient results

- 275 Positive outliers of nitrate, nitrite and ammonium concentrations (from bottle samples obtained from the 111 CTD casts) from within the euphotic zone (~ 0 to 100m) and depth averaged (0 to 100 m) were used to identify areas where significant nutrient concentrations intruded into the euphotic zone. Further analysis of the environment, including several methods of estimating vertical mixing, were used to investigate potential mechanisms that might supply this dissolved nitrogen to the euphotic
- 280 zone. Nitrate was the most abundant dissolved inorganic N species. Over all depths (0 to 2000m) the average nitrate concentration was 3.0 μ M followed by 0.15 μ M for ammonium and 0.08 μ M for nitrite. Over the entire cruise, but restricted to the euphotic zone (defined here as 0 to 100m), the average ± SD nitrate (NO₃), silicate (Si(OH)₄) and phosphate (PO₄) concentrations were 0.26 ± 0.46 (n = 550), 2.42 ± 0.71 (n = 531) and 0.076 ± 0.046 μ M (n = 536), respectively. Nutrient
- 285 concentrations tended to covary with depth and with each other; NO₃, Si(OH)₄ and PO₄ reaching greater than 30, 100 and 2μ M, respectively, at 1000 m (Fig. 4). The relative availability of

dissolved macronutrients deviated significantly from the Redfield (1963) ratios of 16:16:1 (N:Si:P) required by phytoplankton. The excess of $Si(OH)_4$ over NO₃ was considerable, and over all depths, only 11% of samples had N:Si ratios greater than Redfield (greater than 1) while 63% of all

- 290 measurements were < 0.1 or less than Redfield by a factor of 10 (Fig. 4). In the case of PO₄ the excess relative to NO₃ was still extreme, albeit differently distributed. Only 0.6% of all measurements exceeded Redfield (N:P greater than 16) while 34% of all measurements were 10 times less than Redfield (Fig. 4). The average euphotic zone nitrate concentration (0.26 µM) and ratios for dissolved inorganic NO₃:Si(OH)₄:PO₄ of ~ 3:30:1 suggest the likelihood of extreme N
 295 limitation with both Si and P available to phytoplankton in relative excess. The euphotic zone had
- just 20 measurements, or 3.8% of all observations, of $\geq 1 \ \mu$ M nitrate. These locations are investigated further below.

North to south description of nutrient sources in the Leeuwin Current

300 Several features of the LC are described in detail to elucidate the important sources of nutrients and the processes that deliver these to the euphotic zone. At 22°S the continental shelf is very narrow with a prominent low DO layer observed at ~ 175m depth (Fig. 5). This low DO was associated with low salinity water and markedly elevated nitrate concentrations (~8µM) relative to the water above (mean bottle samples $NO_3 = 0.15 \text{ }\mu\text{M} \pm 0.08$). Below this low DO layer, the nitrate 305 concentration went through a minimum at 250m before increasing again at depths exceeding 350m. At 22°S the surface mixed layer was relatively deep (Fig 6C) at the shelf break, considerably deeper than the approximately 40m at 23°S and most locations further south. High rates of vertical mixing were implied by the lack of photoacclimation in photoprotective pigments especially at 22°S (Fig. 6C). The satellite altimetry data reveal the presence of a nearshore, cyclonic or cold-core (CC) eddy 310 at 22°S at the time of sampling (Fig. 3A) a likely factor in accelerating the LC and the deepening of the mixed layer. The surface 150m had a NO₃:Si ratio of ~ 0.03 that increased to 0.77 in the low salinity, high nitrate layer found at ~150 m. The phytoplankton within the eddy at 22°S were deeply

Evidence of thin, shallow layers of low dissolved oxygen and high nitrate off northwest Australia

- At the offshore end (\geq 1000m depth) of the 3 transects at 23, 24 and 25°S there was considerable nitrate (~ 5 µM) present relatively deep (50 to 100m) in the euphotic zone (Fig. 6A, 7). Here the Leeuwin Current (LC) was strongly evident as a warm (approximately 25°C), low salinity (35.2 psu) and high chl*a* (fluorescence) water mass from the surface to approximately 85m at 24°S (station 94, Fig. 7). This surface layer of high velocity, warm, low salinity water is considered as the
- 320 defining feature or core of the LC. Further south at 25°S and still offshore the LC had similar T, S and Fl characteristics but was shallower reaching only to a depth of approximately 50m at 25°S (station 88, Fig. 7). Sharp temperature, salinity, fluorescence, dissolved oxygen (DO) and nutrient gradients were present and below this layer there was a cooler and fresher layer with low DO and high nitrate. At 24°S (Stn 94), and especially at 25°S (Stn 88), it was evident that the concentrations
- 325 of nitrate did not increase uniformly with depth in association with decreasing temperature and increasing salinity (Fig. 7). At station 94 nitrate concentrations reached 8.8 μM at 160m. Nitrate concentrations fell with depth to a minimum at approximately 250m and then rose steadily towards the seafloor (Fig. 7). At station 88 the nitrate concentrations were 5.5 μM at 88m, declined to near zero before a second peak at 205m, declined again towards 250m before eventually rising with
- 330 depth. The horizontal layering of waters with distinct differences in density and fluorescence, nitrate and DO strongly suggest that the greater nitrate concentrations in these layers were not generated by vertical mixing from greater depth.

Forms of dissolved inorganic nitrogen in the euphotic zone and their potential sources

The availability of dissolved inorganic nitrogen to phytoplankton in the euphotic zone at stations 88 and 94 could be assessed from the 6 bottle samples analysed for nutrients between 0 and 100m. At station 88 the depth-averaged nitrate was $0.92\pm2.2 \,\mu$ M while nitrite was $0.04\pm0.07 \,\mu$ M and ammonium was $0.01\pm0.009 \,\mu$ M. Similarly, at station 94 depth-averaged nitrate was $1.0\pm2.2 \,\mu$ M while nitrite was $0.01\pm0.01 \,\mu$ M and ammonium was $0.007\pm0.005 \,\mu$ M. Thus nitrate was 25 to 100 times more abundant than nitrite or ammonium in the euphotic zone and was a potential source of

340 DIN for phytoplankton growth in this northern region.

All of the shallow layers of unusually high nitrate were closely associated with a decline in DO. The bottle samples analysed for nitrate showed very good agreement with the concentrations estimated by the ISUS sensor but the vertical resolution achieved by the latter made the relationships between DO and nitrate much more evident in these relatively thin layers. For these profiles the apparent oxygen utilization (AOU = theoretical O₂ solubility - observed O₂ concentration) was calculated from the classic "Redfield model" (Redfield, 1942). Theoretical solubility was calculated after Garcia and Gordon (1992). These AOUs were then converted into potential DIN assuming respiration of phytoplankton biomass with Redfield (Redfield 1942) ratios of C:N and O:C of 1:1 (Fraga et al. 1998). The predicted DIN concentrations closely replicate the vertical patterns in

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350 nitrate concentrations with only minor overestimations in DIN relative to the measured nitrate values (Fig 7). Thus these relatively shallow (75 to 150 m) peaks in nitrate concentrations were potentially generated by particulate organic matter (POM) remineralized near the base of the LC.

Depth-averaged, euphotic zone nitrate concentrations showed a strong pattern of greatest concentrations along the shelf break with lower concentrations found closer to shore or further

offshore (Fig. 6A). These shelf break stations were selected to coincide with the centre of the LC as determined from Seasoar sections and real time underway surface data. The shelf break stations had depth-averaged euphotic zone (0 to 100m) nitrate concentrations consistently in the range of 0.15 to 0.30 µM NO₃ in the vicinity of the LC. Based on the salinity and temperature derived estimates of mixed layer depth these shelf break stations with greater depth-averaged nitrate concentrations (Fig. 6A) were generally not areas of particularly deep vertical mixing (Fig. 6C). Due to the presence of the LC along the shelf break between 23 and 33°S the mixed layer depths were mostly quite shallow averaging ~ 40 to 60m. In general a surface mixed layer depth of 60m is not sufficient to entrain

nutrients from below the seasonal thermocline in these locations.

Greater ammonium concentrations at mid coast latitudes as evidence for a change in processes.

365 Over the entire cruise and within the euphotic zone (0 to 100m) ammonium was rarely (only 13 of 405 measurements) observed at concentrations exceeding 1μM. These few observations of greater than 1μM ammonium resulted in depth-averaged values (0 to 100m) exceeding 0.3 μM NH₄

between 29 and 32°S and 113 to 114.5°E (Fig 6B). For example at 31°S and in 1000m water the euphotic zone (0 to 100m) had a depth-averaged concentration of 0.78 µM NH₄ and 2

- 370 measurements of greater than 1 µM NH₄ (Fig. 7, station 49). At this offshore location the euphotic zone nitrate concentrations were also elevated relative to inshore and relatively constant from 0 to 100m at 0.33±0.02 µM. The LC was present as a deeper (~ 125m) isothermal and isohaline feature that was significantly cooler and saltier than further north. Vertical mixing as a factor in nitrogen supply to the euphotic zone.
- 375 In general there were very strong vertical gradients in biogeochemical parameters observed at
- the base of surface mixed layer (Fig. 7) indicating that rates of vertical mixing to greater depths were slow relative to phytoplankton growth and nutrient remineralization. Over the duration of the cruise the observed nitrate minima were always deeper than the surface mixed layer (Fig. 7, 8). Even the deepest surface mixed layers with eddies remained isolated by density gradients from the nitrate
- 380 below the seasonal thermocline (see later). Vertical gradients from the surface to 50 m were relatively weak in all parameters at only a few isolated locations: at 22°S (eddy), offshore at 23°S and the eddy at 31°S. Over the entire research voyage the strength of vertical gradients in temperature, salinity, DO, fluorescence and percent transmission over 0 to 50m, 50 to 100m and 100 to 150m were highly correlated (Table 1). In particular the strength of the fluorescence gradient was
- correlated with the gradient in % transmission (P = 2x10⁻¹⁷). Fluorescence gradients were also positively correlated with temperature gradients but negatively with salinity gradients suggesting that fresher, warmer waters at the surface were important factors for the initiation of this shelf scale bloom (Table 1). These gradient results and their interpretation as indicators of vertical mixing were broadly consistent with those estimated from (DT+DD)/chla. There were relatively few stations
 where, based on the ratio of (DT+DD/chla), rates of vertical mixing were rapid, ~ 10 cm s⁻¹ between the chl*a* maximum and the surface (Fig. 6C). These relatively high rates of vertical mixing between the surface and deep chl*a* maximum (DCM) were only observed where the DCM was within the surface mixed layer. For example, in the LC between 22 and 24°S and at 33 and 34°S) and in the eddies at 22°S and 31°S. Excluding the warm core eddy at 31°S (see later) there was relatively little

coherence in the patterns of elevated euphotic zone nitrate concentrations and observations of relatively rapid vertical mixing (Fig. 6A, B, C) between the chla maximum and the surface.
 The warm core eddy at ~ 31°S and its potential sources of dissolved inorganic nitrogen.

A significant deepening of the surface mixed layer was observed in the LC meander that was forming a warm core (WC) eddy during the early portion of the cruise. This feature had formed a

- detached eddy and was moving south east at ~ 7 km d⁻¹ between 16/05/2007 and 31/05/2007. We sampled across this eddy on 22/05/2007 at 31°S and 112.7°E where the mixed layer depth reached ~ 160m. This newly formed and strongly rotating feature with a diameter of greater than 100 km was slightly less saline and slight colder than core LC water and had a much deeper surface mixed layer depth than the surrounding water masses (Fig. 6B). Within this eddy a very large injection of nitrate
- 405 into the euphotic zone had occurred. Relative to the surrounding non-LC water the eddy was warm, fresh, had high concentrations of nitrate and low concentrations of dissolved oxygen (Fig. 8). The adjacent surface waters had nitrate concentrations ranging from 0.1 µM to below detection limit while across the eddy surface nitrate was 0.42 to 0.80 µM. Reflecting the general surplus of Si over N along the west coast of Australia both the surface LC and adjacent surface mixed layer had low
- 410 molar NO₃:Si ratios with an average of 0.03 over 0 50m. Shoreward of the LC there was no source of nitrate (Fig. 8). In sharp contrast the WC eddy had NO₃:Si ratios about 10 times greater, ~ 0.25. The core of the LC upstream of the eddy also had NO₃:Si ratios a long way below 0.25. Based upon our observations it is not possible to create a WC eddy with these N:Si and DO characteristics using water derived from shoreward of the Leeuwin Current (i.e. coastal), from the core of the LC or from
- 415 any other shallow water mass in the vicinity of the eddy. Underneath the eddy there are water masses with greater nitrate concentrations and high N:Si ratios but there is a very significant density gradient between these and the eddy suggesting vertical mixing is not very significant. Relative to the WC eddy at 31°S with its relatively high nitrate and low DO, the eddy observed at 22°S had these characteristics mostly isolated below it
- 420

High resolution sections just upstream of the 31°S eddy show the LC was not homogenous but consisted of multiple 'streams' of differing characteristics (Fig. 9). The surface mixed layer was

~ 100m deep and centred at ~ 113.8°E. Below this was a thin layer of intermediate salinity and low DO between 100 and 150 m (Fig. 9). This thin layer was similar to the low DO, high nitrate, unusual NO_3 :Si observed just below the surface layer of the LC at 23, 24 and 25°S (Fig. 6). The thin layer

- 425 was modestly cooler and fresher than the water above or below it (Fig. 6, 9). The high resolution sections obtained by Seasoar show this to feature to be constrained to immediately below the core of the LC between 29 and 30°S and not an intruding water mass from onshore or offshore (Fig. 9). The Seasoar section also shows a very high degree of spatial variability in the phytoplankton biomass (Fig. 9). Outside the LC and offshore there is a deep chl*a* maximum at ~ 75m. Moving across the LC
- 430 the principal orientation of spatial variability within the euphotic zone is no longer vertical but has become strongly horizontal. Therefore, within the relatively homogenous surface mixed layer of the LC the distribution of phytoplankton biomass shows considerably more horizontal structure than further offshore.

Evidence for a range of nitrogen pathways into the euphotic zone in the southwest.

- Considering a longitudinal section along the shelf break (200 to 300m), approximately the middle of the LC, at 22°S LC salinity was less than 35.2 and the temperature greater than 25.3°C at the surface (Fig. 10). By the time the LC reached 34°S it had cooled approximately 4°C to 21.5°C and increased its salinity by 0.5 to greater than 35.7. This section along the LC also shows the mixed layer depth was shallowest at 26°S and increased north and south of this latitude. It is clear that the LC had lost enough heat and gained enough salt to become similar in density to the water
- immediately below it at latitudes exceeding 26°S (Fig. 10). As the LC erodes into the thin layer of high nitrate water immediately below these nutrients are mixed higher into the euphotic zone. Thus the main source of the nitrate in the euphotic zone of the LC water south of 28° and the source of the nitrate and low DO in the eddy seems likely to be the entrainment of this deeper water into the
- surface mixed layer of the LC.

At most sections south of 28°S the deeper LC showed modestly enhanced concentrations of nitrate throughout the surface mixed layer. Some locations, however, retained the structure of a thin, shallow layer of high nitrate and low DO even as far south as 32°S (Fig. 11). At this latitude the

section shows a thin layer of high nitrate, low DO that is below a very weak salinity and temperature 450 induced density gradient (0.1 ppt and 0.1°C). At ~ 70m this nitrate is within the euphotic zone. South of 28°S and near the Abrolhos Islands there was also broad rise in euphotic zone ammonium concentrations to a depth averaged ~ 0.3 μ M (Fig. 6). In these areas the euphotic zone ammonium concentrations also showed considerable variation with depth (Fig. 7, station 49) but often tended to be greater than nitrate at latitudes between 29 and 32°S. The longitudinal section (Fig. 10) along the

455 shelf edge shows these latitudes to overlap with the peak in chl*a* concentrations between 28 and 34°S.

At the far southern end of the western continental shelf the oceanography was again quite complex. There was a cold core eddy near 114°E with drifter in it (Fig. 3) and considerable

- 460 meandering by the LC which was still evident as an increase in sea surface temperature relative to ~ $21.2^{\circ}C$ (Fig. 3). Shoreward of the LC the surface temperature dropped to $20.2^{\circ}C$ and the mixed-layer extended all the way to the seafloor while the rate of vertical mixing was relatively high (Fig. 12 and 5, respectively). At these near shore locations the concentrations of NO₃ were unusually homogeneous with 0.86 μ M, the greatest surface concentration observed throughout the voyage,
- found at the shallowest station (~ 50m, Fig. 12). Surface silicate concentrations were also high but across the entire transect (n = 8) where they averaged 2.11 ± 0.1 (SD) μ M. The near-shore depthaveraged (0 to 41 m) N:Si ratios were also high (0.43, SD = 0.030) and consistent with the values found under the core of the LC. The near shore dissolved oxygen concentrations were close to saturation at 228 μ M suggesting they must have become oxygenated.

470 Discussion

Unlike most eastern boundary currents the LC arises in the tropics and is warm, fresh, buoyant, geostrophically-driven and poleward flowing. During winter the LC is easily identifiable as a ~ 50 to 100m deep layer of uniform temperature and salinity with high silicate, phytoplankton and low DIN moving rapidly southward off the west coast of Australia. In spite of its apparently low

- 475 DIN the peak in LC flow coincides with a shelf scale bloom over ~ 500000 km² (Moore et al. 2007). The source of nitrogen to fuel the annual shelf-scale bloom has been hypothesized to be from the pool of dissolved inorganic nutrients found below the seasonal thermocline and brought into the euphotic zone via enhanced vertical mixing possibly associated with autumnal deepening of the surface mixed layer (Feng et al. 2009). More LC flow during La Niña years (positive SOI) is
- 480 associated with increased fisheries production (Caputi 2008, Caputi et al. 2001) and greater phytoplankton biomass (Koslow et al. 2008) along the west Australian coast. Based on 40 years of monthly data on the continental shelf the warmer water during winter is correlated with greater nitrate concentration (Thompson et al. 2009), a trend that is the reverse of those found in most other locations (Switzer et al. 2003).
- 485 During the 2007 cruise there was no evidence that deep mixing into the seasonal thermocline was the dominant mechanism suppling nutrients to eddies or the euphotic zone south of 23°S. On the contrary the most likely source of nutrients to support the Australian west coast bloom was a thin layer of water with low dissolved oxygen and high nitrate concentrations (LDOHN) immediately under the core of the Leeuwin Current. A similar thin layer of low DO at about 200m has been
- reported in the Indian Ocean from 0 to 25°S at 75E (Wyrtki 1971, Warren 1981), by Rochford
 (1969) at 110°W and under the northern region of the LC by Woo and Pattiaratchi (2008). Offshore of NW Australia this LDOHN layer was found as shallow as 50m and well separated from the nitrate found below the seasonal thermocline by depth and substantial differences in density (herein). Similarly, at low latitudes, the low DO layer was clearly distinct from water above by very strong
- 495 gradients in temperature, salinity and fluorescence (herein, Woo and Pattiaratchi 2008). Within the

LDOHN layer the apparent oxygen utilization was stoichometrically sufficient to provide the observed concentrations of nitrate and suggests relatively high and rapid rates of POM decomposition may supply this DIN. The very sharp gradients in physical and biogeochemical parameters indicate very little vertical mixing at these lower latitudes. Although we did not measure

- 500 these POM to DIN fluxes the physical arrangement of high chla just above the low DO, high DIN layer makes it feasible that local phytoplankton represent the source of POM undergoing decomposition and remineralisation. Alternatively the POM or DIN may have accumulated in this layer over time and have being funnelled into the base of the LC. At 23°S the LC flows south at 0.6 m s⁻¹ but the shallowest LDOHN layer was just underneath the core of the LC between 50 and 100m
- 505 and was moving at one third the velocity (E. Weller, pers. comm.). The California Current (Ward et al. 1989) also has layers of LDOHN but the geographic extent and the high concentrations of nitrate within this relatively shallow N recycling layer observed off Western Australia appear unprecedented. That the thin LDOHN layer was broadly present underneath the LC off NW Australia and then southward under the LC provides a novel explanation for the shelf scale
- 510 phytoplankton bloom and the other ecological impacts of the variation in LC strength.

Thin layers of nitrite have been reported near the base of the chl*a* maxima with some controversy regarding whether it is due to excretion by phytoplankton or the slow conversion of nitrite to nitrate (Lomas and Lipschutz 2006). The relatively low concentrations of NH₄ and NO₂ observed off north western Australia may be an artefact of relatively sparse bottle sampling which could miss a very thin layer; or unusually efficient nitrification. The lack of observed NO₂ and NH₄ plus the near balance between the apparent oxygen utilization and NO₃ pool favours the latter, efficient conversion of POM into nitrate; e.g. POM \rightarrow NH₄ \rightarrow NO₂ \rightarrow NO₃. We suggest the strong vertical structure allows a highly-structured and tightly-coupled community of amonifiers and nitrifiers to develop under favourable conditions, with sufficient POM near the base of the euphotic zone but still in warm conditions. Thin layers of biota have been reported in a range of ecosystems

including coastal shelves (Cowles & Desiderio 1993), fjords (Holliday et al. 1998, Dekshenieks et al. 2001), and open ocean waters (Bjornsen & Nielsen 1991, Carpenter et al. 1995) but there is

relatively little known about the vertical distributions of nitrifying bacteria and Archea or Crenoarchaeota (Beman et al. 2008, 2010). The magnitude and speed of the proposed N cycling

- 525 implies Crenoarchaeota for ammonification (Francis et al. 2005) and the reduction in DO with the paucity of NH₄ or NO₂ suggests the possibility of heterotrophic Crenoarchaeota for the nitrification step (Wuncher et al. 2008). As in other instances of shallow water nitrification the nitrate produced is suggested to be an important source of N for primary production (Wankel et al. 2007). The first survey of ammonium concentrations off the west Australian coast (herein) showed NH₄
- 530 concentrations were generally lower than NO₃ with only a few localized exceptions.

Warm core eddies are most often low in biomass and productivity (Biggs 1982) but off west Australia they are have more biomass and are more productive than surrounding waters (Thompson et al. 2007). Based on modelling and satellite data the source of nutrients for these eddies has been suggested to be from the coastal zone (Dietz et al. 2009). The data presented here demonstrate that

- 535 in 2007 there was no source of coastal zone water with low DO, sufficient nitrate or suitable N:Si ratio to supply these eddies; nor did there appear to be any offshore source of water with these characteristics. Deeper waters in the region do have the right characteristics but remain well isolated from the surface mixed layer of the WC eddies by strong density gradients and there was relatively little evidence that significant 'pumping' occurred from below the seasonal thermocline
- 540 (McGillicuddy and Robinson 1997). Mixing into the thin layer under the core of the LC seems to be the most likely source of nitrate for the eddies observed at 22 and 31°S.

South of 28°S the surface layer of the LC has become considerably denser (both cooler and saltier) and in some instances appears to have mixed through the deeper LDOHN layer. In 2007 this newly formed and deeper surface mixed layer meandered westward to form a high-biomass warm-core eddy containing significant DIN in the surface mixed layer (herein). A similar process was observed in 2006 (Paterson et al. 2008) and these eddies are more productive than the surrounding water masses (Thompson et al. 2007). As the LC pushed past 28°S it carried elevated DIN as nitrate and ammonium plus ~ $0.3 \,\mu g \, chla \, L^{-1}$ within the euphotic zone. Elementary stoichometry would suggest this DIN was sufficient to double or triple the existing standing stock of chl*a* and therefore

- support the observed annual phytoplankton bloom off Perth (~ 32° S). At these higher latitudes the LC was sometimes mixed deeply enough to entrain the LDOHN layer but it could also contain this layer within the euphotic zone. Either scenario provides an answer why warmer winter waters are associated with a rise in surface nitrate concentrations from ~ 0.1 to 0.3 µM at Rottnest Island (55m depth, 32.2°S, Thompson et al. 2009).
- The deepening of the LC south of 28°S was associated with intense horizontal flow, high latent heat loss, high eddy kinetic energy (Feng et al. 2003) and more intense vertical mixing. These processes can generate considerable phytoplankton patchiness (Abrahams 1998). Along the LC from 22 to 34°S the variation in vertical mixing rates estimated from photoprotective pigments was largely sub mesocale. Seasoar sections showed much greater small scale variability than previously
- 560 reported for the LC (e.g. Woo and Pattiaratchi 2008). The distributions of phytoplankton biomass from onshore to offshore showed biological responses were occurring along the edges of the current flow (e.g. Levy et al. 2001) suggesting mixing along isopycnal edges of the LC flow. The hypothesized small scale of this vertical mixing provides a possible explanation for the patchiness of the biological responses observed off the west coast (e.g. Hanson et al. 2005).
- 565 South of 28°S there was a broad rise in euphotic zone ammonium concentrations. The shift from nitrate to ammonium as the primary source of DIN in the water column between 29 and 32°S (excluding the WC eddy) indicates some considerable change in the relative importance of the major pathways of N cycling at these latitudes. It is suggested that an increase in vertical mixing may disrupt the tight coupling between the microbial communities that undertake both ammonification
- 570 and nitrification within the LDOHN layer in this region. Further south, off the southwest corner of Australia, there was elevated nitrate present throughout the water column. The source of this DIN cannot be ascribed with certainty as the water masses below 34°S were not characterised. The surface flow was northward and it is possible the Capes Current was flowing inside of the LC (Gersbach et al. 1999, Hanson et al. 2005) or a large recirculation due to the presence of a mesoscale
- 575 eddy. The temperature, salinity, nitrate and silicate characteristics of the water suggests the shelf was flooded with LC water that had been mixed to a depth of ~ 130m before being pushed onto the shelf.

ACCEPTED MANUSCRIPT In conclusion, the discovery of a thin layer of high nitrate and low DO (LDOHN) water

underneath the core of the LC provides a novel explanation for the shelf scale phytoplankton bloom along the west coast of Australia. The available evidence suggests a shallow, warm and buoyant LC

580 creates conditions that favour rapid and shallow nitrification. The ultimate source of the organic matter used in this remineralisation remains unresolved.

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Table 1. Correlation coefficients for gradients (Δ) in selected physical, chemical and biological water properties. For each station the change in property (Δ) was calculate from surface to 50 m, from 50 to 100 m and from 100 to 150 m (n = 212 to 214). For each property the *correlation* (r^2 value),

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 probability (P) value are given in italics, normal text, respectively. Highly correlated properties have similar vertical structure.

 Image: structure dissolved salinity itemperature oxygen is solved itemperature itempera

	dissolved	salinity	temperature	%
	oxygen			transmission
Fluorescence	0.0969	-0.208	0.376	-0.537
	0.160	0.00231	0.000000163	2.3x10 ⁻¹⁷
Dissolved		0.208	0.0750	-0.135
oxygen		0.00233	0.277	0.0494
Salinity			0.00234	0.219
			0.973	0.00136
Temperature				-0.167
				0.0149



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Figure 1. A conceptual representation of the strengthening Leeuwin Current (LC) and entrainment of thin layers of low dissolved oxygen (DO) and high nitrate concentrations as observed during late autumn 2007. At the latitudes of 22 to 25°S the LC is warmer and fresher than surrounding waters with strong vertical gradients in temperature, salinity, oxygen, fluorescence and nitrate observed
between 50 and 80 m. Just below this there were thin layers of low DO and high nitrate (red colour). The northern or western extent of these thin layers was not determined but they appear to be entrained into the LC at depth. Southwards and near the Abrolhos Islands the Leeuwin Current narrows along the shelf edge, has cooled, and has high eddy kinetic energy. South of the Abrolhos Islands the LC produced a large warm core eddy observed off the shelf at ~ 31°S with relatively high nitrate (purple colour) and low dissolved oxygen plus N:Si ratios all indicating the source of these waters to result from entrainment of this thin layer into the euphotic zone. Farther south, off Perth (~32°S), the LC existed in 2 modes. One mode with nitrate from this thin layer now mixed to the surface (purple colour) and another with the thin layer still intact but at relatively shallow depths (~

70m).

Accempting



Figure 2. A) Calibration of the dissolved oxygen sensor on the CTD with bottle samples determined by Winkler type titrations. B) Nitrate concentrations measured in bottle samples (x axis) versus potential nitrate concentrations estimated assuming that the oxygen deficit was converted into nitrate at molar ratios of 6.6:6.6:1 for O:C:N.

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Figure 3. (A) A composite image of sea surface height (white lines at 0.1m contours), sea surface temperature (colours) and current velocities (arrows) estimated from calculated geostrophic flow (David Griffith, pers. comm.) for May 22 2007. (B) Cruise track and shipboard ADCP estimates of current velocities (red arrows) in upper 8m. (C) inset showing seasonal chl*a* from SeaWiFs (R2009) for 2007 and climatology (1997 to 2010) for region in papel B. Cruise duration is shown by solid





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Figure 4. All nutrient concentrations from the entire cruise (Fig. 6B shows locations) over all depths from the surface to 2000 m with just 20 nitrate concentrations above $100m \ge 1 \mu M$. Lower panels show histograms for frequency of NO₃:Si(OH)₄ or NO₃:PO₄ ratios versus number of observations on log₁₀ scales with dashed vertical lines representing Redfield ratios and dotted lines Redfield/10. Note the majority of samples are greater than 10 times below Redfield indicating the likelihood of severe nitrogen limitation. Lower right panel shows nitrate versus silicate with the unusual combination of high nitrate and low silicate concentrations that are found just under the Leeuwin Current (in the ellipse).

(colour on web, black and white in print)



Figure 5. A section at 22°S from near shore to 1000m water depth showing contours for dissolved oxygen (μ M). Stations were undertaken at triangles. Solid white line is the vertical profile from nitrate sensor at the offshore station (113.7°E) with concentrations from bottle samples (X). Dashed white line is vertical profile for chl*a* (from calibrated fluorescence) at mid shelf station (113.8°E).

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Figure 6. Depth averaged (0 to 100 m) nutrient concentrations from each CTD station, estimated (rates of vertical mixing, cruise track, CTD stations and mixed layer depths. Panel (A) contours for depth averaged (0 – 100m, bottle samples, n ~ 6) nitrate concentrations (μ M) and bubble plot of all nitrate concentrations (bottle samples) from 0 to 100 m (bubble size is proportional to

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665 Concentration). Three specific CTD stations (94, 88, 49) are labelled and shown in detail in Fig 7. Line between 30°S ~ 115°E and 29°S, 113.2°E is seasoar section shown in Fig 8. Panel (B) Cruise track (black line), CTD station locations (thin X), contour plot for depth averaged (0 to 100 m, bottle samples, n ~ 6) ammonium concentrations (μM). Panel (C) Contour plot of mixed layer depths (m)

and bubble plot of estimates of mixing rates (cm s⁻¹) based on ratios of photoprotective pigments

Acceleration

670 (see Material and Methods for details of calculation).

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Figure 7. CTD profiles at 24°S (stn 94), 25°S (stn 88) and 31°S (stn 49) see Fig. 6A for locations. All three panels have identical scales. NO₃ estimate is the potential nitrate concentration estimated if apparent oxygen utilization was converted into nitrate at molar ratios of 6.6:6.6:1 for O:C:N. Arrows indicate layers of low dissolved oxygen and high nitrate at relatively shallow depths. At Station 94 there is a broad peak in nitrate and low DO from 100 to 250m. At Station 88 there are similar layers between 50 and 100m and again between 150 and 250m. At Station 49 the LC had deepened to 100m and no layers of low DO & high nitrate were observed. In all instances high fluorescence was observed in the LC.

(colour on web, black and white in print)



Figure 8. Section along 31°S transect showing (A) buoyant Leeuwin Current water at the shelf edge, ~ 114.8°E; also an eddy at ~ 112.6 °E (density, sigma_t = kg m⁻³ -1000). (B) dissolved oxygen (μ M). (C) nitrate (μ M from calibrated ISUS sensor). (D) NO₃:Si(OH)₄ ratios. The only observed source of water with high nitrate, low dissolved oxygen and high NO₃:Si(OH)₄ ratios was ~ 100m deep under the Leeuwin Current upstream of the eddy (white crosses indicate bottle samples and profile location). (colour on web, black and white in print)



Figure 9. Section composed from hundreds of CTD profiles made by the Seasoar towed from inshore
at 30°S 114.6°E to offshore at 31°S 113.3°E (see Figure 6A). (A) is temperature (°C), (B) is salinity,
(C) is chla from calibrated fluorescence (D) is dissolved oxygen (µm l⁻¹) from sensor. A layer of low
(~ 180 µm l⁻¹) dissolved oxygen between 60 and 120m is clearly evident under the warm water of
the Leeuwin Current and discrete from onshore or offshore waters.

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Figure 10. Longitudinal section along continental shelf edge (200 m) showing vertical gradients of temperature, salinity, nitrate, fluorescence (Chl*a*) and dissolved oxygen (DO). One or more vertical profiles at each degree of latitude were used to construct the contours. Top panel shows mixed layer depth at individual stations as a bar (-) and joined by a dotted black line.

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Figure 11. Sections at 32°S from near shore to 1000m water depth. (A) Nitrate section from sensor showing thin layer of high nitrate under core of Leeuwin Current. (B) Dissolved oxygen section with low dissolved oxygen at base of LC, (C) Temperature showing LC generally warmer than inshore or offshore at this latitude, (D) Salinity section showing some modest stratification at ~ 60m depth in the LC. Red triangles indicate locations of CTD profiles.

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Figure 12. Section at 34°S. (A) shows contoured density (sigma t, density in kg m⁻³ -1000). (B) shows contoured nitrate (μ M) from ISUS sensor. Red triangles show locations of CTD profiles.

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Research highlights

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• Unusually shallow nitrification in eastern Indian Ocean

- Leeuwin Current structure and flow are factors in nitrification
- Shelf scale phytoplankton bloom results from these nutrients
- Anticyclonic eddies in the southeast Indian Ocean derive their nutrients from base of Leeuwin Current

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