Biological oxygen production from oxygen-to-argon ratios and oxygen isotopologues in the Atlantic Ocean

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Thesis submitted for the degree of Doctor of Philosophy
University of East Anglia, UK

November 2012

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Abstract

Marine primary producers play an important role in controlling the atmospheric carbon dioxide through photosynthesis and export of organic matter into the deep ocean. In this thesis I used two biogeochemical techniques based on O₂/Ar ratios and O₂ isotopologues to measure net community production (N) and gross oxygen production (G) in two different areas relevant for the marine C cycle: the South Atlantic subtropical gyre and the North Atlantic during a spring bloom. The former despite small rates of production it is relevant for the global marine C cycle due to the large area it covers; in addition the study of this gyre may contribute to clarify the ongoing debate on whether subtropical gyres are net autotrophic or heterotrophic. The North Atlantic is a main component of the global C production because of the large the amount of C that is fixed during the spring bloom. N was estimated from continuous measurements of O₂/Ar ratios with a Membrane Inlet Mass Spectrometer and G from discrete samples both in the USW of RSS James Cook (South Atlantic) and R/V Knorr (North Atlantic). Discrete samples were processed in a newly built gas extraction line and analyze in an Isotope Ratio Mass Spectrometer at UEA. The gas extraction line was built for the separation of O₂ and Ar from N₂ without isotopic fractionation. This thesis shows that the South Atlantic Gyre produced O₂ at a rate of 10±3 mmol m⁻² d⁻¹ in March/April 2009, thus was net autotrophic. Interestingly G (177±96 mmol m⁻² d⁻¹) was much higher than previous estimates. This difference could be due to other processes that might fractionate the O₂ without fixing any carbon such as the Mehler reaction. Measurements of N made in the North Atlantic during a spring bloom in May 2008 showed the highly variable and heterogeneous nature of the area. Within the bloom N had an average value of 67 mmol m⁻² d⁻¹ with N increasing from 60 to 170 mmol m⁻² d⁻¹, followed by a short period of net heterotrophy and finishing at 5 mmol m⁻² d⁻¹. These changes were associated with changes in the species composition, with diatoms dominating first followed by the increase of nanophytoplankton. These techniques show O₂/Ar and O₂ isotopologues to be useful and accurate proxies for production with the potential for complete automation of O₂/Ar measurements.
I would like to express my sincere appreciation and gratitude to my supervisors Jan Kaiser and Dorothea Bakker. They both contributed with ideas that shaped this project. I was amazed by Jan’s ability to find clever solutions in the office, lab and at sea, but I especially appreciate his sharp intellect, his attention to detail and the little pushes he gave me when I needed them. Dorothea Bakker dedicated many hours to discuss specific details of my work, and I thank her especially for always being available for advice and lending a hand when needed.

I also would like to give special thanks to Johanna Gloël, lab-partner and officemate, who became a great friend; she was of incredible help and support in all the aspects of my thesis. Her incredible common sense was always of great help! During the writing up of my thesis, Sue Palminteri became my editor. Her dedication and patience greatly improved my writing skills.

In the lab I am indebted to many people but especially to Alina Marca Bell, who introduced me to the insides of Isotope Ratio Mass Spectrometry. Also I highly appreciate the time and assistance that Osamu Abe dedicated to me while building the extraction line used in this study. I also want to thank all the technicians either from the Stable Isotope Lab or not, which were always available to lend a hand: Andy Macdonald, Stephen Woodward and Paul Disdle.

In the office to all the people that allowed me to distract them in 01.37K. Starting with the ones I distracted the most (just because they were sitting closer to me): Sophie Chollet, Johanna Gloel, Michal Bochenek, Rachel Gibson, Jan Strauss, Cansu Bayindirli, Phil Wilson, Michelle Fernandes, Paul Lancaster, Rafaella Nobili and in the old times Janina Woeltjen, Marie Racault, Amandine Caruana, Claire Powel, Nuno Nunes and Mat Jones. Also thanks to the friends from offices afar which would agree to have lunch in Igmac, especially to Maria Martinez de Alvaro which brought back the Spanish spirit that I was beginning to loose, Tiziana Luisetti, Mi Tian, Maria-José Marin Altaba, Christiana Faria, and Maribel Velasco. And also to all the friends that left UEA before me but without whom this PhD would not have been the same: Clara Moyano, Agnieszka Latawiec, Sue Palminteri and Karel Castro-Morales.
At sea I would like to thank the Principal Investigators that allowed me to take part on both cruises: Mary Jane Perry and Brian King. I am indebted to many people that helped me during the cruises, in particular Nicole Bale, Nathan Briggs, Giorgio Dall’Olmo, Toby Westberry, Sinhue Torres, Mark Moore, Niki Silvera and Steve Woodward.

An “¡OLÉ!” to my family. They always have been supportive and understanding throughout this whole process. Starting with my parents without whom I would never have started this PhD, but also thanks to my brother Miguel, as well as all my other sisters and brothers and to all my little sobrininos.

A very special thank you to Charlene and Alan Lobo who basically adopted me and took care of me especially in the final stages of the thesis. I cannot say a thank you big enough for everything they did for me showing me all the warmth from Spain with a Goan accent.

And a warm thanks to Lorenzo who encouraged me to always see the bigger picture and whatever the weather always was there for me.
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1.1. Relevance of the ocean in the global carbon cycle

Carbon dioxide (CO₂) is one of the most important anthropogenic greenhouse gases in the atmosphere. Since the industrial revolution the concentration in the atmosphere has been steadily increasing due to the input by human activities such as fossil fuel use and cement production.

However, only 40% of the CO₂ emitted by human activity has remained in the atmosphere. The rest has been absorbed by land and ocean reservoirs. The oceans store 50 times more CO₂ than the atmosphere and 17 times more than the land biosphere (Denman et al., 2007).

Marine carbonate chemistry is believed to play an important role in controlling the concentration of CO₂ in the atmosphere (Takahashi et al., 1993). The following processes control the distribution of CO₂ in the ocean: the solubility of CO₂ (solubility pump), the carbonate chemistry, ocean circulation and biological removal from the euphotic zone to deeper waters (biological pump).

Dissolved inorganic carbon (DIC) is composed of the inorganic carbon species dissolved CO₂, carbonic acid (H₂CO₃) bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻). When CO₂ gas enters in the ocean, it reacts in a series of equilibrium reactions that form H₂CO₃, HCO₃⁻ and CO₃²⁻:

\[
\begin{align*}
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+
\end{align*}
\]

The solubility pump (Volk and Hoffert, 1985) results in transport of inorganic carbon from the surface of the ocean to its interior. This pump acts in cold dense waters that sink to the deep ocean, carrying large amounts of dissolved inorganic carbon (DIC) and isolating them from the surface.

The biological pump (Volk and Hoffert, 1985) is fuelled by photosynthesis in the surface ocean. Photosynthesis is carried out by autotrophic organisms, transferring CO₂ into organic matter. A simplified reaction equation of photosynthesis is
\[ n \text{CO}_2(aq) + n \text{H}_2\text{O} + h\nu \rightarrow n\text{O}_2 + (\text{CH}_2\text{O})_n \]

The organic matter formed could either sink or be transported by the thermohaline circulation to deeper layers and therefore be removed from contact with the atmosphere (biological pump) or could be respired or remineralised.

\[ n \text{O}_2 + (\text{CH}_2\text{O})_n \rightarrow n \text{CO}_2 + n \text{H}_2\text{O} \]

\( \text{CO}_2 \) is produced during respiration and consumed during photosynthesis; \( \text{O}_2 \) behaves inversely so that their concentration changes are opposite to each other. When disregarding the physical effects of the solubility of \( \text{O}_2 \) in the water, \( \text{O}_2 \) can be used as a biogeochemical tracer for net community production (\( N \)) (Craig and Hayward, 1987; Emerson, 1987; Spitzer and Jenkins, 1989). The \( \text{O}_2 \) produced by photosynthesis is called gross oxygen production (\( G \)). \( N \) is equal to \( G \) minus community respiration (\( R \)).

### 1.2. Areas of study

This thesis presents data from two different regions of the Atlantic Ocean. The first region is the North Atlantic during the spring bloom. The second region is the oligotrophic South Atlantic gyre in the austral autumn season.

Despite covering only 15\% of the global ocean area, the North Atlantic accounts for 23\% of the total oceanic uptake of anthropogenic carbon (Sabine et al., 2004). From a biological point of view the North Atlantic is relevant because of the large amount of \( \text{CO}_2 \) that is fixed during the spring bloom and then exported to the deep ocean. This bloom is special in a way that the magnitude of the export which occurs is not comparable to other areas in the world.

Oligotrophic subtropical gyres occupy about 40\% of the earth surface. These oceanic "deserts" are characterized by low concentrations of nutrients and low rates of photosynthesis. Because of their sheer size they are nevertheless relevant for global carbon budgets. Currently there is an ongoing debate whether these big open ocean areas are net sources or sinks of \( \text{CO}_2 \) to the atmosphere (Ducklow and Doney, 2013). On the one hand, Duarte et al. (2013) consider oligotrophic areas as net heterotrophic ecosystems. In contrast
to Williams et al. (2013) that consider them to be net autotrophic. While Duarte et al. (2013) suggest that these areas are supported by organic carbon inputs from the continental shelf, nutrients from the atmosphere or by non-photosynthetic autotrophy and mixotrophic metabolic pathways. Williams et al. (2013) argues that these areas must be net autotrophic because in situ O₂ methods despite their uncertainties show autotrophy (they might be wrong in the quantity but not in the sign), because the observed ¹³C enrichment in DIC could only be explained by positive N and because neither horizontal or vertical transport and mixing nor atmospheric inputs of organic matter would be sufficient to support these communities.

Specifically, it is not clear whether the South Atlantic is a net source or sink of CO₂. Studies determining the metabolic balance of this region with bottle incubations gave mixed results. Net heterotrophy was found by González et al. (2002) in spring and autumn and by Gist et al. (Gist et al., 2009) in autumn only, whereas Serret et al. (2006) and Gist et al. (2009) found net autotrophy in spring.

1.3. Production measurements in the ocean

Different methodologies to measure the productivity in the ocean measure different properties and these will be explained first.

**Gross production** is the total organic matter produced by photosynthesis without any respiratory losses. It is related to the transfer of electrons from H₂O to the terminal electron acceptor, CO₂. It might be expressed in terms of amount of C fixed in amount of O₂ produced. However, there are some photobiological reactions such as photorespiration or the Mehler reaction that produce O₂ without C fixation.

**Respiration:** This includes all processes which transfer electrons from organic matter to O₂ with the subsequent production of CO₂. Respiration can be carried out by autotrophs and heterotrophs. Thus, **net primary production** is the difference between gross production and autotrophic respiration; and **net community production** is gross production minus all respiratory processes by autotrophs and heterotrophs (Falkowski and Raven, 1997).

There are several techniques to measure organic matter production in the ocean and thus different terms to define production in the ocean. They can be separated into in vitro methods where bottle incubations are used to determine the different rates and in situ methods where production is determined from specific biogeochemical tracers in the region of
study. The main in vitro measurements are: $^{14}$C incubation, $H_2^{18}$O incubation, $^{15}$N incubation and dark and light $O_2$ bottle incubations.

$^{14}$C incubations are widely used as a productivity measurement technique. Described by Steeman Nielsen (1952) the method consists of adding $^{14}$C-labelled DIC to the sample and incubating for 12-24 h at ambient or simulated ambient light levels (to capture all production over a diurnal cycle) or <2 h at multiple light levels (to derive a production-irradiance flux curve, which is then used to work out integrated production rates). There are some caveats when using this methodology as photorespiration, remineralisation of particulate organic carbon (PO$^{14}$C) and dissolved organic carbon (DO$^{14}$C) excretion can lead to a low bias in measured production rates (Bender, 1999; Williams and Lefevre, 1996). Thus, the measurements performed by this method are considered to represent something in between gross and net production, and they are often referred to as "$^{14}$C primary productivity". Also, being an incubation method, it suffers from bottle effects such as the reduction of autotrophs during incubation time (Calvo-Díaz et al., 2011; Fernández et al., 2003), the increase of heterotrophs (Calvo-Díaz et al., 2011) or the exclusion of grazers (Bender, 1999), which can introduce both low or high biases in the desired production rates.

$H_2^{18}$O incubations consist of incubating samples with spiked water ($H_2^{18}$O) and measuring the proportion of $^{18}$O present in the dissolved $O_2$ in the water at the end of the incubation period (Bender et al., 1987). The advantage of this technique over the $^{14}$C method is that the pool of $O_2$ is much larger than that of POC and thus $^{18}$O labelled-$O_2$ is less likely to be recycled than PO$^{14}$C (Bender et al., 1999). The disadvantage is that like the $^{14}$C measurements it is an in vitro method with the associated problems. Furthermore, there are processes that are not fixing any carbon but increase the amount of $^{18}$O-labelled $O_2$ such as the Mehler reaction (Bender et al., 1999).

$^{15}$N assimilation studies consists of the incubation of a sample injected with a compound (usually nitrate or ammonium) with a known $^{15}$N signature. The incorporation of this compound into the particulate organic nitrogen pool is used to measure new production (this means NO$^3_-$ based production) or recycled production (this means NH$^+_4$ based production) (Neess et al., 1962). Like the other methods mentioned above, this in vitro method might suffer from bottle effects.

$O_2$ bottle incubations are based on differences of in vitro dissolved $O_2$ changes between light and dark incubated bottles (Gaarder and Gran, 1927). This method aims to measure net community production, gross production and community respiration.
In situ methods on the other hand, provide measurements that are not biased by incubation techniques. Examples are remote measurement of chlorophyll $a$ concentrations from satellites; mixed layer budgets of different compounds ($O_2$, $NO_3^-$, DIC, thorium $^{234}$Th) and fast rate repetition fluorescence (FRRF).

Satellites chlorophyll production estimates using remotely sensed chlorophyll fluorescence are calibrated with $^{14}$C primary production measurements (Behrenfeld and Falkowski, 1997). This is a useful tool as it can give estimates on a world-wide scale unachievable by other techniques that often only provide snapshots of production rates at the exact sampling time and place. However, the $^{14}$C method has drawbacks associated with it. For example, depending on incubation conditions and sampling location, the derived production estimates may lie somewhere between net and gross primary production. Also, the satellite only measures chlorophyll concentrations in the top-most surface layer and these measurements are not very accurate in areas where coloured dissolved organic matter (CDOM) concentrations are high (Arrigo et al., 2011). Additionally, chlorophyll concentrations are not a direct measure of carbon fixation rates since carbon-to-chlorophyll ratios may vary according to species and other factors.

Fast rate repetition fluorometer analysis aims to determine photosynthesis rates (gross primary production) by measuring the physiological state of photosystem II (Kolber et al., 1998) (PS II). It looks at the electron flow through PS II (Suggett et al., 2001). The disadvantage of this method is that the electron flow through PS II is not only dependent on photosynthesis rates, but it also depends on phytoplankton community composition as well as nutrient limitation (Suggett et al., 2009).

Net community production can be inferred from budgets of $O_2$, DIC, $^{234}$Th deficiencies and nutrient inventories (Bender et al., 1992; Buesseler et al., 1992; Chipman et al., 1993; Emerson, 1987). Their advantage is that they measure actual in situ properties and are inherently unbiased by incubation artefacts. However, their use requires the budgets of these compounds to be well characterized in terms of physical transport and time trends, as well as, in the case of $O_2$, wind-speed gas exchange parameterisations, which may have significant uncertainties.

Recently, two new techniques to measure net ($N$) and gross ($G$) oxygen production in the mixed layer from measurements of $O_2$/Ar and $O_2$ isotopes have been developed. They have the advantage that they are in situ methods and therefore do not suffer from bottle effects. They also require less sampling and processing time compared to in vitro methods. Another advantage of these methods is that they integrate over the residence time of the gases in the
mixed layer and are therefore representative of longer time periods compared to other techniques, which might miss short-lived production spikes. However, vertical mixing with waters below the mixed layer or horizontally sometimes have to be taken into account where there are significant \( O_2 \) gradients.

### 1.4. Use of \( O_2/Ar \) and \( O_2 \) isotopes for the measurement of net and gross production

#### 1.4.1. Net community production measured by \( O_2/Ar \) ratios

Craig and Hayward (1987) described the use of oxygen and argon as an indicator of net community production based on the similar solubilities and diffusivities of these gases. This means that both are similarly affected by physical processes like bubble injection and changes in barometric pressure and temperature. However, \( O_2 \) takes part in biological processes (photosynthesis and respiration) while Ar is an inert gas, which means that it has no biological sources or sinks.

Therefore the \( O_2/Ar \) ratio can be used to separate \( O_2 \) supersaturation into a biological and a physical component (Craig and Hayward, 1987; Spitzer and Jenkins, 1989). Biological supersaturation, \( \Delta(O_2/Ar) \), expresses \( O_2 \) supersaturation in excess of Ar supersaturation and can be written as:

\[
\Delta(O_2/Ar) = \frac{c(O_2)/c(Ar)}{c_{sat}(O_2)/c_{sat}(Ar)} - 1
\]

where \( c(O_2)/c(Ar) \) represents the ratio of concentration of \( O_2 \) and Ar; \( c_{sat}(O_2)/c_{sat}(Ar) \) is the ratio of the saturation concentration of \( O_2 \) (Garcia and Gordon, 1992) and Ar (Hamme and Emerson, 2004).

Based on this, the biological \( O_2 \) air-sea flux \( (F_{bio}) \) is defined as (Kaiser, 2005):

\[
F_{bio}(O_2/Ar) = \Delta(O_2/Ar) \cdot k_w \cdot c_{sat}(O_2)
\]
where \( k_w \) is the weighted gas transfer coefficient which is calculated taking into account the wind speed history of the water following Reuer et al. (2007). Positive \( F_{bio} \) values correspond to loss from the oceanic mixed layer.

\[ F_{bio} \]

\[ F_{bio} \text{ can be considered to be equal to } N, \text{ assuming steady state and neglecting vertical and horizontal exchange of } O_2 \text{ and } Ar. \]

\[ N = F_{bio} \quad (1.3) \]

A breakthrough in the measurements of \( N \) based on \( O_2/Ar \) was achieved by the continuous measurements of \( O_2/Ar \) using membrane inlet mass spectrometry (MIMS). MIMS was developed by Kana et al. (1994) and it has been used widely in several oceanographic studies, e.g. Kaiser et al. (2005), Tortell et al. (2005b), Gueguen et al. (2008) and Nemcek et al. (2008). The short term reproducibility of the \( O_2/Ar \) ratio measurement is 0.05% Kaiser (2005).

MIMS consist of a semipermeable membrane that allows the extraction of the gases dissolved in the water, which are then led to a quadrupole mass spectrometer for analysis. The semipermeable membrane separates a liquid phase and a vacuum gas transfer line connected to a quadrupole mass spectrometer. The sample (liquid phase) is constantly brought to the membrane by a water pump. When the sample reaches the membrane, a portion of the gas in the water enters the vacuum due the difference of pressure between the liquid phase and the vacuum gas phase. A schematic view of this system is depicted in Figure 1. Gas molecules are brought to an ionization chamber where they are ionized and sent to the flight tube where they are selected according to their mass/charge ratio \((m/z)\) by a specific radio-frequency. This radio-frequency is tailored to a specific \( m/z \), so that ions of this \( m/z \) going through the flight tube are directed to the detector. The changes in radiofrequency through the rods of the mass spectrometer allow collecting different \( m/z \) ratios. The fast shifts of this radiofrequency allow measurement of 20 different ions every 10 s.
1.4.2. Gross Production

$\text{O}_2$ has three stable isotopes: $^{16}\text{O}$, $^{17}\text{O}$ and $^{18}\text{O}$, which differ in their number of neutrons with 8, 9 and 10 neutrons, respectively. The most abundant isotope is $^{16}\text{O}$ with an abundance of 99.758%, followed by $^{18}\text{O}$ with 0.204% and $^{17}\text{O}$ with 0.038%. Isotope abundance is normally reported as delta ($\delta$) quantities with the abundance ratio of the heavier isotope over the lighter isotope versus a known reference. This is expressed as:

$$\delta_{\text{sample/ref}} = \frac{R_{\text{sample}}}{R_{\text{ref}}} - 1 \quad (1.4)$$

$$R = \frac{c(\text{O})}{c(^{16}\text{O})} \quad (1.5)$$

The superscript * on $\delta$, $R$ and $\text{O}$ represents the isotopes $^{17}\text{O}$ or $^{18}\text{O}$. $R_{\text{sample}}$ and $R_{\text{ref}}$ are the ratio of abundance of isotopes $^{18}\text{O}$ or $^{17}\text{O}$ over the $^{16}\text{O}$ in the sample and reference respectively. For these studies the preferred reference is tropospheric air.

The change in isotopic composition through a process from B to A like photosynthesis, respiration, gas evasion or gas invasion can be expressed with the fractionation ($\varepsilon$):


\[ \delta^*_{A-B} = \frac{\delta^*_A - \delta^*_B}{1 + \delta^*_B} \]  

Where \( \delta^* \) stands again for the isotope of study, in this case \(^{18}\)O or \(^{17}\)O; \( \delta \) expresses the \(^{18}\)O/\(^{16}\)O or \(^{17}\)O/\(^{16}\)O anomaly in the state A or B as indicated by the subscripts.

Luz and Barkan (2000) found that the isotopic composition of oxygen can be used to trace the gross production in the ocean. The method is based on the different isotopic composition of the oxygen gas in the air, \( O_2 \) and the oxygen in the water molecule \( H_2O \). This isotopic anomaly of \( O_2 \) in the air comes from the non mass dependent fractionation in the reactions of \( O_2 \) and \( CO_2 \) in the troposphere and stratosphere (Lämmerzahl, 2002; Thiemens et al., 1995; Yung et al., 1991) which results in a depletion of \(^{17}\)O in atmospheric \( O_2 \), which is different from the isotopic composition of oxygen in the water molecule \( H_2O \). Marine photosynthesis produces dissolved \( O_2 \) which carries the isotopic signature (with a small fractionation) of water. This contrasts with the isotopic signature of dissolved \( O_2 \) coming from air-sea exchange. Therefore the analysis of \( O_2 \) isotopes dissolved in water can be an indicator of marine oxygen production.

Following Luz and Barkan (2000) and Kaiser (2011b), excess \(^{17}\)O in dissolved \( O_2 \) in seawater with respect to atmospheric \( O_2 \) is calculated as:

\[ 17\Delta = 17\delta - \gamma_R 18\delta \]  
\[ \gamma_R = 17\varepsilon_{R/18}/18\varepsilon_R \]

\( 17\Delta \) represents the dissolved \( O_2 \) measured excess of \(^{17}\)O versus atmospheric air; \( 17\delta \) and \( 18\delta \) represent the anomaly of \(^{17}\)O and \(^{18}\)O versus air respectively; \( \gamma_R \) is the expected mass dependant fractionation for the respiration fractionation ratio of \( 17\varepsilon_R / 18\varepsilon_R \).

Generally \( 17\delta \) and \( 18\delta \) are expressed in per mill (‰) and \( 17\Delta \) in parts per million, that is ppm (note that some authors use per meg, which is the same as ppm). Luz and Barkan (2000) propose the calculation of the dimensionless gross oxygen production rate (\( g \)) as the ratio of the gross oxygen production (\( G \)) over the gas gross \( O_2 \) influx from the atmosphere:
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(1.9)

\[ g = \frac{G}{k_w \cdot c(O_2)} \]

(1.10)

\[ G = k_w \cdot c(O_2) \cdot g \]

Where \( k_w \) is the weighted gas transfer coefficient or piston velocity.

Luz and Barkan proposed \( g \) to be approximated by the ratio of the difference between the dissolved \(^{17}\text{O}\) excess and saturated \(^{17}\text{O}\) excess value over the difference between the \(^{17}\text{O}\) excess only due to photosynthesis and the dissolved \(^{17}\text{O}\) excess:

(1.11)

\[ g_{LB} = \frac{(^{17}\Delta_{\text{dis}} - ^{17}\Delta_{\text{sat}})}{(^{17}\Delta_{p} - ^{17}\Delta_{\text{dis}})} \]

where \(^{17}\Delta_{\text{dis}}\) is the \(^{17}\Delta\) measured in the samples, \(^{17}\Delta_{\text{sat}}\) is the \(^{17}\Delta\) when the \( O_2 \) present in the water is only due to exchange with the atmosphere and biological processes are negligible and \(^{17}\Delta_{p}\) is the value in a system, where there is no exchange with the atmosphere and the \( O_2 \) is only formed by biological activity.

In 2011, Kaiser (2011b) and Prokopenko et al. (2011) independently within 8 days of publication proposed the calculation of \( g \) without any mathematical approximation. Both calculations are very similar and their only difference is that Prokopenko et al. (2011) do not take the small fractionation during invasion and evasion of \( O_2 \) from air-sea gas exchange (\(*\varepsilon_i\) and \(*\varepsilon_e\)) into account. For this work is adopted the calculation of \( g \) as defined by Kaiser (2011b, equation 48), \( g_K \) as it is considered to be more accurate from a theoretical point of view.

(1.12)

\[ g_K = \frac{(1 + \Delta(O_2))\left(^{17}\varepsilon_E - \gamma_R ^{18}\varepsilon_E\right) - ^{17}\varepsilon_i - ^{17}\delta}{1 + ^{17}\delta} + \gamma_R \frac{^{18}\varepsilon_i - ^{18}\delta}{1 + ^{18}\delta} \]

(1.13)

\[ \Delta(O_2) = \frac{c(O_2)}{c_{\text{sat}}(O_2)} - 1 \]
where $\Delta(O_2)$ is the saturation anomaly of $O_2$, calculated as in equation 1.12 with the in situ concentration of $O_2$, $c(O_2)$, and the saturation concentration of $O_2$, $c_{sat}(O_2)$, at in situ conditions (Garcia and Gordon, 1992). $\varepsilon_{I_1}^{17}O$, $\varepsilon_{E_1}^{17}O$, $\varepsilon_{I_2}^{18}O$, $\varepsilon_{E_2}^{18}O$ are the invasion and evasion isotopic fractionation of $O_2$ at invasion and evasion of $^{17}O$ and $^{18}O$ respectively with the temperature at in situ conditions. $\delta^{17}O$ and $\delta^{18}O$ are the measured anomalies in the sample of $^{17}O$ and $^{18}O$; $\delta^{17}O_p$ and $\delta^{18}O_p$ are the isotope delta $^{17}O$ and $^{18}O$ of photosynthetic $O_2$; and $\gamma_R$ is the expected mass dependant fractionation for respiration fractionation ratio of $\varepsilon_{I_1}^{17}O / \varepsilon_{E_1}^{17}O$.

**Description of parameters use for the calculation of $g$:**

As explained, $\gamma_R$ is the expected fractionation for respiration; this was measured by Luz and Barkan (2005) to be 0.5179. It can also be defined as the kinetic respiratory slope for the dominant $O_2$ consumers in aquatic systems and thus represents the ratio between the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotope effects in ordinary respiration (Luz and Barkan, 2005). $\gamma_R$ is obtained from the slope of the linear relationship of $\ln(1+\delta^{17}O)$ versus $\ln(1+\delta^{18}O)$ for respiration in a closed system. This value substitutes the value of 0.516 of Angert et al. (Angert et al., 2003) which was only applicable for dark respiration through the cytochrome pathway, even though some authors still use it, e.g. Reuer et al. (2007).

$17\Delta_{sat}$ is the $^{17}O$ excess when a parcel of water is in equilibrium with the atmosphere. This is calculated as defined by Luz and Barkan (2009):

$$17\Delta_{sat} = \ln (1 + 17\delta_{sat}) - \lambda \ln (1 + 18\delta_{sat})$$  \hspace{1cm} (1.14)

$17\delta_{sat}$ and $18\delta_{sat}$ are the saturation delta of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ respectively and are explained in detail later; and $\lambda = 0.518$ which is the (rounded) ratio between the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotope effects which represents global respiration (Luz and Barkan, 2005).

$17\Delta_{sat}$ has been measured by several studies and has been reported with values from 4 ppm to 18 ppm (Kaiser, 2011b, table 1). The reason for the disagreement between these measurements is not clear (Stanley et al., 2010) It is possible that temperature might play a role in these differences but it would not explain all. Following Kaiser (2011b in the current research the temperature-dependent value reported by Luz and Barkan (, 2009 #105) was chosen.
Chapter 1. Introduction

The saturation delta value, $^{18}\delta_{\text{sat}}$, and its dependence on temperature was measured by Benson et al. (1979, table VIII row 2) and is described in equation 1.15.

$$^{18}\delta_{\text{sat}} = e^{-0.00072951 + 0.42696 / (T/K)} - 1$$  \hspace{1cm} (1.15)

Where $T$ is the temperature in Kelvin.

Following Kaiser (2011b), $^{17}\delta_{\text{sat}}$ is back-calculated with equation 1.14 and 1.15 and $^{17}\Delta_{\text{sat}}$ reported by Luz and Barkan (2009).

Fractionation of the $^{18}\text{O}/^{16}\text{O}$ during evasion ($^{18}\varepsilon_{E}$) was measured by Knox et al. (1992) to be (-2.8±0.2) ‰. As in Kaiser (2011b) the rest of the parameters of the kinetic fractionation during evasion and invasion are calculated with the $^{*}\delta_{\text{sat}}$ and the $^{18}\varepsilon_{I}$ (Kaiser, 2011a; Kaiser, 2011b).

$$^{18}\varepsilon_{I} = (1 + ^{18}\varepsilon_{E})(1 + ^{18}\delta_{\text{sat}}) - 1$$  \hspace{1cm} (1.16)

$$^{17}\varepsilon_{I} = (1 + ^{18}\varepsilon_{I})\kappa$$  \hspace{1cm} (1.17)

$$^{17}\varepsilon_{E} = \frac{^{17}\varepsilon_{I} - ^{17}\delta_{\text{sat}}}{1 + ^{17}\delta_{\text{sat}}}$$  \hspace{1cm} (1.18)

$\kappa$ is the triple isotopic fractionation of invasion and was assumed to be (0.516±0.015) covering the theoretical predicted mass dependent range of isotope effects (Kaiser, 2008).

Calculation of the photosynthetic delta $^{*}\delta_{p}$ depends on the photosynthetic fractionation ($^{*}\varepsilon_{p}$) and the isotopic composition of the oxygen in the water ($^{*}\delta_{w}$) (Kaiser and Abe, 2012).

$$^{*}\delta_{p} = (1 + ^{*}\delta_{w})(1 + ^{*}\varepsilon_{p}) - 1$$  \hspace{1cm} (1.19)

For the isotopic composition of sea water relative to atmospheric $\text{O}_2$, there are three studies with uncertainties in $^{17}\delta_{\text{VSMOW}}$ smaller than 0.05 ‰, Barkan and Luz (2005), Barkan and Luz (2011) and Kaiser and Abe (2012). They report the delta values of the international
standard Vienna Standard Mean Ocean Water (*$\delta_{\text{VSMOW}}$) relative to Air-O$_2$. $^{18}\delta_{\text{VSMOW}}$ is assumed to equal the isotope delta of mean sea water ($^{18}\delta_{\text{sw}}$). $^{17}\delta_{\text{sw}}$ is 5 ppm depleted relative to $^{17}\delta_{\text{VSMOW}}$.

The three studies cited above do not agree in their $^{*}\delta_{\text{VSMOW}}$ values. The values reported by Barkan and Luz in 2005 and 2011 are $^{17}\delta_{\text{VSMOW}}\text{(B&L05)} = (-11.931\pm0.010) \‰$ and $^{18}\delta_{\text{VSMOW}}\text{(B&L05)} = (-23.320\pm0.020) \‰$; $^{17}\delta_{\text{VSMOW}}\text{(B&L11)} = (-11.883\pm0.012) \‰$ and $^{18}\delta_{\text{VSMOW}}\text{(B&L11)} = (-23.324\pm0.017) \‰$ and for Kaiser and Abe (2012), $^{17}\delta_{\text{VSMOW}}\text{(K&A)} = (-12.102\pm0.040) \‰$ and $^{18}\delta_{\text{VSMOW}}\text{(K&A)} = (-23.647\pm0.030) \‰$. It is not clear yet what the reason is for the difference, but Kaiser and Abe (2012) point out that the B&LO5 comparison between two international reference standards SLAP (Standard Light Antarctic Precipitation) vs. VSMOW is different from previous widely accepted measurements (Gonfiantini, 1977, 1978). Thus in this thesis, the values of $^{*}\delta_{p}$ using the values from Barkan and Luz (2011) and Kaiser and Abe (2012) (Table 1) are reported.

Fractionation during photosynthesis, $^{*}\varepsilon_{p}$, has been reported to differ for different species (Eisenstadt et al., 2010; Helman et al., 2005). In total they describe five species which are listed in Table 1 which are *Synechocystis* (Helman et al., 2005, cyanobacteria), *Nannochloropsis oculata* (Eisenstadt et al., 2010, Eustigmatophyte), *Phaeodactylum tricornutum* (Eisenstadt et al., 2010, diatom), *Emiliania huxleyi* (Eisenstadt et al., 2010, coccolithophore) and *Chlamydomonas reinhardtii* (Eisenstadt et al., 2010, green alga). Kaiser and Abe (2012) mention that previous measurements of the fractionation during photosynthesis of $^{18}$O/$^{16}$O, $^{18}\varepsilon_{p}$, have shown little fractionation for *Phaeodactylum tricornutum* (Guy et al., 1993) in contrast with the values reported by Eisenstadt (2010); as well as contradicting theoretical values of Tcherkez and Farquhar (2007). The values of Eisenstadt et al. (2010) and Helman et al. (2005) are currently the only available data for both $^{17}\varepsilon_{p}$ and $^{18}\varepsilon_{p}$ at the moment. Here is used the biological end-member delta value as suggested by Kaiser and Abe (2012) and Barkan and Luz (2011) from the specific species $^{*}\delta_{p}$ values (Table 1).
Table 1: Photosynthesis fractionation $\varepsilon_p$ reported in the literature for different species and associated $\delta_p$ for these species. $\delta_p$ are reported according to $\delta_{VSMOW}$ as measured by Barkan and Luz (2011) and Kaiser and Abe (2012). Averages of all the species $\delta_p$ for each of the $\delta_{VSMOW}$ are also reported.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\varepsilon_p$</th>
<th>$\delta_p$</th>
<th>$\varepsilon_p$</th>
<th>$\delta_p$</th>
<th>$\varepsilon_p$</th>
<th>$\delta_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synechocystis</td>
<td>0.250</td>
<td>-11.860</td>
<td>17 $\varepsilon_p$</td>
<td>-11.641</td>
<td>18 $\delta_p$</td>
<td>-22.868</td>
</tr>
<tr>
<td>Nannochloropsis oculata</td>
<td>1.496</td>
<td>-10.629</td>
<td>17 $\delta_p$</td>
<td>-10.410</td>
<td>18 $\delta_p$</td>
<td>-20.540</td>
</tr>
<tr>
<td>Phaeodactylum tricornutum</td>
<td>2.314</td>
<td>-9.821</td>
<td>17 $\delta_p$</td>
<td>-9.601</td>
<td>18 $\delta_p$</td>
<td>-19.001</td>
</tr>
<tr>
<td>Emiliania huxleyi</td>
<td>3.050</td>
<td>-9.094</td>
<td>17 $\delta_p$</td>
<td>-8.874</td>
<td>18 $\delta_p$</td>
<td>-17.646</td>
</tr>
<tr>
<td>Chlamydomonas reinhardtii</td>
<td>3.653</td>
<td>-8.498</td>
<td>17 $\delta_p$</td>
<td>-8.278</td>
<td>18 $\delta_p$</td>
<td>-16.448</td>
</tr>
</tbody>
</table>

Average: $\varepsilon_p = -9.980$, $\delta_p = -19.625$

1.5. Overview of research

The aim of this thesis is to understand marine biological production in two distinct areas of the Atlantic Ocean: one in the North Atlantic during a spring bloom and other in the subtropical gyre in the South Atlantic. The objective is to use two relatively new techniques to estimate $N$ and $G$ in surface waters by continuous measurements of $O_2$/Ar ratios and discrete of $O_2$ isotopologues.

In Chapter 2 is presented an automated custom-made $O_2$ and Ar extraction line built jointly by my fellow PhD student Johanna Gloël and me. This was used for the analysis of discrete samples for their analysis of $O_2$ isotopologues and $O_2$/Ar ratios. The work is based on the work of Barkan and Luz (2003) with some modifications. The line is capable of measuring one standard and six samples in a single run, with all the processes controlled remotely by a computer.

In Chapter 3 are described the methods used for the collection, analysis, and calibration of the data used for this PhD research.

In Chapter 4 are presented continuous measurements of $O_2$/Ar ratios and discrete oxygen triple isotope measurements in the South Atlantic gyre in the austral autumn of 2009. From these measurements is estimated net and gross production and discussed the metabolic balance of the gyre as well as comparing them with previous in vitro estimates of net and gross
production. Also are related the results of this study to ancillary data like surface chlorophyll concentrations, nutrient concentration, and fast repetition rate fluorometer data.

In Chapter 5 are presented continuous oxygen concentration data as well as discrete triple oxygen isotope data and O₂/Ar for the North Atlantic Bloom Experiment in May 2008. High spatial heterogeneity is found in the bloom. The data is used to discuss estimates of net production based on different techniques. Results from this study are compared with results from Quay et al. (2012) and Alkire et al. (Alkire et al., 2012) that were obtained during the same experiment. With the help of a Lagrangian float to indicate a specific patch of the bloom, is evaluated the data for different stages of the bloom and the evolution of its species composition.

In Chapter 6 are described the general conclusions of this thesis and are discussed future research priorities.
Chapter 2. Custom built gas extraction line
2.1. Introduction

The aim of the gas extraction line is to obtain O₂ (oxygen) and Ar (argon) from seawater samples for later analysis. This is done by extracting the gas phase from the seawater samples and by removing H₂O (water vapour), CO₂ (carbon dioxide) and N₂ (nitrogen).

At the end of the extraction process, the O₂ and Ar gases are cryogenically collected on molecular sieve pellets for later analysis with an isotope ratio mass spectrometer (IRMS). H₂O, CO₂ and N₂ gases need to be removed because they can interfere with the O₂ analysis in the IRMS. The presence of N₂ increases the measured ¹⁷δ value. The CO₂ might fake the presence of N₂, when there is none because the CO⁺ fragment generated from CO₂ in the ion source is isobaric with N₂. H₂O adheres to the interior surfaces of the mass spectrometer and reacts with the gases present in the mass spectrometer, thus reducing the signal.

This extraction line was built jointly with another PhD student, Johanna Gloël, under the supervision of Jan Kaiser. The line that we built is presented in this chapter and was based on the design of Barkan and Luz (2003), with some modifications. These modifications were: 1) The gas chromatographic (GC) column for the separation of the N₂ was put at 0 °C in our case versus -80 °C in the original design; 2) We added an extra initial preparation step of the samples on which the sample was extracted from the sampling bottles and collected into glass tubes with molecular sieve; 3) We used a different setup, which included a 10 port-2 position valve instead of four 3-port 2-position valves. 4) The amount of samples per run was 7 instead of 10. 5) Processed samples are not frozen in liquid helium but in molecular sieves on liquid nitrogen. Most of the building, programming and tests in the line were done jointly by Johanna Gloël and myself (unless otherwise stated), but the following method description and all analyses are entirely my own.

2.2. Preparation line for the extraction of gas phase and removal of H₂O

The first preparation step was to extract most of the water from the bottles. The majority of the gas sample is at this point in the headspace of the bottle. This was done by connecting the bottle upside down to a container under vacuum with a maximum pressure of 10 mbar. This way, as much water as possible was extracted without affecting the headspace.

After this preparation step the samples were passed manually through a preparation line. The H₂O vapour left was removed by two traps: one surrounding the sample bottle (T0)
and the other trap (T1) on the way to the collection vial. Each collection vial had 5 molecular sieve pellets (=0.04 g/pellet of 5 Å pore size, grain size 80-100 mesh) at liquid N\textsubscript{2} temperature (-196 °C) where the gas sample was trapped. The procedure was as follows: the sample bottle was put into an isopropanol bath with dry ice at –78 °C (T0) and was connected to the preparation line. The reason that the temperature for traps T0 and T1 was -78 °C and not at liquid nitrogen temperature is that otherwise O\textsubscript{2}, Ar and N\textsubscript{2} might be adsorbed on ice at liquid N\textsubscript{2} temperatures (Barkan and Luz, 2003). The neck of the sample bottle was evacuated until the pressure in the line was below 5 × 10\textsuperscript{-4} mbar as measured by gauge G0 in the line. The valve to the pump was closed and the valve of the bottle was opened. The initial pressure was recorded by G0. Once the vial was opened the sample started to freeze onto the molecular sieve in the vial at liquid N\textsubscript{2} temperature. This setup was kept for approximately 15 min, until at least 99.5 % of the sample was frozen on the molecular sieve. Then the vial was closed and disconnected for later use on the O\textsubscript{2}-Ar extraction line on the same day.

Figure 2.1: Diagram of the preparation line

2.3. The O\textsubscript{2}-Ar extraction line

2.3.1. Description of the O\textsubscript{2}-Ar line

The O\textsubscript{2}-Ar line consists of several parts which can be grouped according to their function as the four different stages of sample treatment: I) sample inlet, II) removal of CO\textsubscript{2}, III) removal of N\textsubscript{2} and IV) collection of samples.
Chapter 2. Custom built gas extraction line

I) Inlet:

Up to 7 vials can be connected to the inlet (Figure 2.2). Each vial connects via a Cajon Ultra Torr fitting to a springless diaphragm valve (6LVV-DPS5-C, Swagelok) with a pneumatic actuator. Each valve is connected to the system with 1/4" stainless steel tubing (SS) and Swagelok fittings. Only one vial at a time is open to the extraction system.

![Figure 2.2: Schematic view of the extraction line with positions of valves (V), traps (T), pressure gauges (G1, G2 and G3), gas chromatographic column (GC), and pumps (LV, low vacuum diaphragm pump and HV, high vacuum turbo pump). Cold traps, V309-312 for moving dewars up and down.](image)

II) Removal of CO₂:

Cryogenic trap, T2 (Figure 2.2) is used for the removal of CO₂ from the samples. The T2 glass trap is kept at -196 °C (liquid N₂) for freezing out the CO₂ in the sample. The trap is connected to the rest of the line with Cajon fittings. A pressure Pirani gauge (G1) located after T2 is used to record the movement of the gas.
III) Removal of $\text{N}_2$

Two traps (T3 and T4) and a gas chromatographic column (GC) are used for the removal of $\text{N}_2$. The traps are kept at either -196 °C or 60 °C as desired. A gas chromatographic column between the traps separates the $\text{O}_2$ and $\text{Ar}$ from the $\text{N}_2$. All these items are connected via a 2-position 10-port valve (Valco, A4L10UWM).

The traps T3 and T4 are built of 1/4” stainless steel tubing and filled with 5Å 80-100 mesh molecular sieve pellets with glass wool at both ends. When V205 is opened, the sample goes through the VALCO valve, is transferred to T3 which at this stage is -196 °C, while G1 records the movement of the sample. After most of the sample is frozen over on T3 (when the pressure in G1 is <0.5% of initial pressure), the Valco valve is changed to the second position and a flow of purified helium (He) at 8 ml min$^{-1}$ is passed through T3, which is then heated to 60 °C by a heating tape. The He is grade CP (99.999 %) and is further purified on a 1.8 m-long column at -196 °C containing 45/60 mesh size molecular sieve 13X (Supelco). The sample is subsequently released from the molecular sieve in T3 to the chromatographic column held at 0 °C (Supelco, 13130-U).

The column allows the He to pass freely, while retaining $\text{O}_2$, $\text{Ar}$ and $\text{N}_2$. Retention times for $\text{O}_2$ and $\text{Ar}$ are similar while the retention time for $\text{N}_2$ is longer. This difference in the retention time allows to separate the $\text{O}_2$ and $\text{Ar}$ from the $\text{N}_2$. Both $\text{O}_2$ and $\text{Ar}$ go to T4 where they are adsorbed on the molecular sieve at -196 °C while the He flows out of the extraction system via a waste line. This waste line has sufficient volume (120 ml) to avoid any back flush from the room air to the line. After the $\text{O}_2$ and $\text{Ar}$ have been released from the column and trapped on T4, the 10-port 2-position valve is switched again so that the $\text{N}_2$ can go to waste while the high vacuum pump removes the excess He while retaining the $\text{O}_2$ and $\text{Ar}$ from T4 at -196 °C.

IV) Collection of the samples:

In the final stage T4 is isolated from the high vacuum pump and heated to 60 °C. One of the collection valves is opened and the sample starts to freeze in a collection tube, which has 0.05 g of molecular sieve (5Å 80-100 mesh size) and is kept at liquid $\text{N}_2$ temperature. The change in pressure due to the movement of the sample is recorded with the Pirani pressure gauge G2. After 5 min, most of the sample (>99.5 %) has frozen on the collection tube and the valve to the collection tube in the manifold is closed. After the sample has been collected, the
2.3.2. Automation of the O₂-Ar extraction line

The processes in the O₂-Ar extraction line were controlled from a computer running LabView (National Instruments, Texas, USA). This software is a graphical programming environment that allows controlling hardware as well as giving orders and taking measurements in the O₂-Ar line. The hardware consists of a chassis that connects a computer to the line through four modules. Two of these modules are the NI digital output modules which are used to send electrical signals that have two functions, first to control the temperature control box (in charge of heating the traps T3 and T4 when commanded by the program, see (Table 2.1) and secondly to control the 3 Clippard boards (EMC-12), which supply compressed air when commanded for opening/closing valves as well as for lowering/lifting the dewar vessels for T3 and T4 (Figure 2.3). The two other modules have an analogue input, one for reading voltages from thermocouples (for temperature) and the second one for reading voltages from the pressure gauges and the flow meter. The 10 port-2 position valve is switched by first opening valve V207 (or V208) and closing it 3 s later.

![Figure 2.3: Schematic of the electronics wiring in the line with the data acquisition chassis](image-url)
Chapter 2. Custom built gas extraction line

The fully automated extraction procedure consisted of a step-by-step command sequence case structure, which had the following steps:

1. Open valves V202, V203, V204, V205, V206, V209 and V210, while the position of the Valco valve is on 208 (counter clockwise position, CCW). The traps T3 and T4 are exposed to the high vacuum pump.

2. The software reads the pressure in G1, G2 and G3. If the readings are below 5 x 10^{-4} mbar for G1 and G2 and below 1.2 x 10^{-7} mbar for G3 the extraction can start. At this stage valves V203, V205 and V209 are closed. At the same time V309 and V311 are opened, which elevates the jacks with the dewars with LN\textsubscript{2} to immerse T3 and T4.

3. Open one of valve V10\textsubscript{X} of the sample (this can be any value from V101-V107).

4. Open V205 and the sample starts to freeze on T3. Maintain settings for 15 min.

5. Close V210 and open V209 and V207. V207 actuates the VALCO 10-port 2-way to the CW position, V207 is closed after 3 s but the CW position in the Valco remains such that the He flows through T3 until V210 (which has been kept closed) with He gas building up for 4 minutes in the line.

6. After this, open V210, so He flows to waste while the sample is kept in T3 adsorbed on the molecular sieve at -196 °C (liquid N\textsubscript{2} temperature).

7. After 2 minutes the He flow has become stable again. The dewar on T3 is lowered and T3 starts to be heated to 60 °C such that the sample on it is released and goes via the GC column (kept at 0 °C) to T4 (kept at -196 °C LN\textsubscript{2} temperature).

8. After 14 min V210 is closed and the VALCO valve is changed to the CCW position (by opening V208 and closing it after 3 s). T4, which is kept at -196 °C with LN\textsubscript{2} retains O\textsubscript{2} and Ar while the excess He is pumped away.

9. After 5 minutes of pumping, V204 is closed and V312 is opened such that the dewar surrounding T4 is lowered.

10. Start heating T4 to 60 °C. The corresponding valve on the collection manifold V30\textsubscript{X} (any of V301-V307 but analogous to the inlet valve V10\textsubscript{X}) opens and starts the freezing of the sample on the collection manifold which is at -196 °C. This lasts 5 min (when >99.5% of the sample has been frozen) into the collection finger.

11. Once the sample is frozen, valve V30\_ is closed and V202-V206 and V209-V210 are opened. The line is evacuated for 30 minutes and T3 and T4 are heated at 180 °C before a new run can start.
Table 2.1: Key parts and equipment in the O₂-Ar line.

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
<th>Model</th>
<th>Description</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubing</td>
<td></td>
<td></td>
<td>1/4” Stainless steel tubing</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1/8” Stainless steel tubing</td>
<td></td>
</tr>
<tr>
<td>Connections</td>
<td></td>
<td></td>
<td>1/4” and 1/8” Swagelok fittings</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6 mm Cajun fittings</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Filters for glass wool in T3 and T4</td>
<td></td>
</tr>
<tr>
<td>Cold traps</td>
<td></td>
<td>T1, T2</td>
<td>Cryogenic glass trap</td>
<td>Filled with mol sieve and glass wool stoppers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T3, T4</td>
<td>Cryogenic stainless steel trap</td>
<td></td>
</tr>
<tr>
<td>VALCO valve</td>
<td>1</td>
<td>A4L10UWM</td>
<td>10 port 2 position valve, air actuated</td>
<td>Separation of O₂, Ar and N₂</td>
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<tr>
<td>Valves</td>
<td>22</td>
<td>6LVV-DP5S-C</td>
<td>Springless Diaphragm Valves</td>
<td></td>
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<tr>
<td>Flow meter</td>
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<td>AWM 3150V</td>
<td>Reads the flow</td>
<td>Shows the flow of O₂, Ar and N₂</td>
</tr>
<tr>
<td>Chromatographic</td>
<td>1</td>
<td>13074-U</td>
<td>45/60 molecular sieve 5A (Supelco), 9 ft</td>
<td>Separation of O₂, Ar and N₂</td>
</tr>
<tr>
<td>column</td>
<td></td>
<td>13069-U</td>
<td>45/60 Molecular Sieve 13X (Supelco)</td>
<td>Purify the He carrier gas</td>
</tr>
<tr>
<td>Clippar d</td>
<td>3</td>
<td>EMC-12</td>
<td>Control of valves and lab jacks</td>
<td></td>
</tr>
<tr>
<td>Rope heaters</td>
<td>3</td>
<td>M2174/0295</td>
<td>Heating T3 and T4</td>
<td>Connects pressure gauges and module</td>
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<tr>
<td>Pressure reader</td>
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<td>TPG 256 A</td>
<td>Display and management of pressure readings</td>
<td>Connects pressure gauges and module</td>
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<tr>
<td>Pressure gauges</td>
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<td>IKR 251</td>
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<td>National Instruments</td>
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<td>Digital output</td>
<td>Control of EMC-12 and temperature control box</td>
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<td>1</td>
<td>NI cDAQ-9174</td>
<td>Chassis</td>
<td>Transmission of the modules to computer</td>
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</table>
2.3.3. Experiments to identify the optimal settings for the $\text{O}_2$-$\text{Ar}$ extraction

The optimal timing for transferring the sample from vial to T3 and for transferring the sample from T4 to the collection manifold was found to be five minutes. In that time at least 99.5% of the initial sample pressure measured by G1 and G2 was frozen on T3 and the collection manifold.

The appropriate time for opening V210 after switching over (step 6 in the automation) was determined by me as follows: Figure 2.4 shows flow speed for an aliquot of $\text{O}_2$-$\text{Ar}$ mixture which was frozen on T3 and then transferred to T4. The major differences between the chromatograms relate to the time when valve V210 was opened and He was allowed to flow to T4. As shown in Figure 2.4b there is no major difference in the chromatograms of the He flow independently of the time when V210 is opened.

Reverse flow through the flow meter can occur after opening valve V210 when the evacuated trap T4 fills up with He. The rate and duration of reverse flow decrease when the delay between switching over the 10-port valve and opening V210 is increased. This means that while V210 is closed, the accumulation of He gas avoids the creation of this negative flow. In the case of 4 minutes (see Figure 2.4a), the flow is positive directly after opening V210.

![Figure 2.4: Chromatograms of aliquots of $\text{O}_2$-$\text{Ar}$ when frozen on T4. Red circled areas show the time at which V210 was opened.](image)
Johanna Gloël and Chris Brown determined the optimal temperature of the GC column. They found after several tests at different temperatures that at 0 °C the peaks of O₂ and Ar were separated sufficiently from N₂ for a reasonably rapid separation.

The exact retention times of O₂, Ar and N₂ on the GC column were determined as follows: T4 was left at room temperature, such that all the gases leaving from the column would directly go to waste and be recorded by the flow meter. In Figure 2.5, it can be seen that O₂ and Ar elute at the same time for both air and the O₂-Ar mixture. They are released between minutes 6.5 and 12.5 after heating T3. N₂ is released between 18 and 31 minutes, leaving a safe window for collecting the O₂ and Ar between 12.5 min and 18 min. We used 14 minutes in order to minimize contamination from N₂ as well as the duration of a run.

![Chromatogram of N₂, O₂-Ar mixture and dry air after going through the gas chromatographic column indicating the retention times for O₂-Ar and N₂.](image)

**Figure 2.5:** Chromatogram of N₂, O₂-Ar mixture and dry air after going through the gas chromatographic column indicating the retention times for O₂-Ar and N₂.

### 2.3.4. Performance tests of the line

Several tests were done in order to evaluate the performance in the line. These tests look at how different processes could cause isotopic fractionation, that is, change the isotopic composition of a sample going through the line. In order to do this, first it was evaluated how much the isotope ratio mass spectrometer (IRMS) could fractionate the samples. Secondly it was tested how samples would be affected by using the collection manifold and freezing them
in molecular sieve in the stainless steel tube. Thirdly it was evaluated the line itself by passing an aliquot of O₂–Ar gas mixture through the line in the same way as a sample, and then measured it in the IRMS versus the same unprocessed O₂–Ar mixture. Finally, the reproducibility was tested by passing several aliquots of the same dry air gas.

All these tests were evaluated by looking at the relative difference between a working reference (O₂–Ar mixture) and the sample. For the ¹⁷O and ¹⁸O isotopes this is be defined as:

\[ {^*\delta} = \frac{{^*R_{\text{sample}}}}{{^*R_{\text{ref}}}} - 1 \]  \hspace{1cm} (2.1)

with \[ ^*R = \frac{{c(\text{O})}}{c(\text{O}_{16})} \] \hspace{1cm} (2.2)

where * stands for 17 and 18 for the ¹⁷O¹⁶O and ¹⁸O¹⁶O isotopologues of O₂. ¹⁶O in the formula stands for O₂ formed by the two light isotopes ¹⁶O, and ref refers to the working reference.

The relative difference in O₂/Ar ratios (m/z 32 for ¹⁶O₂ and m/z 40 for Ar) is:

\[ \delta_{\text{sample/work, ref}}(\text{O₂/Ar}) = \frac{{R_{\text{sample}}(32/40)}}{{R_{\text{ref}}(32/40)}} - 1 \] \hspace{1cm} (2.3)

The first test looked at the fractionation of the O₂–Ar mixture in the IRMS. It was done by comparing the same gas on standard and reference side (zero enrichment). This showed us that the IRMS was fractionating the sample, but to a very small degree (Table 2.2, row 1), which was within the precision of the instrument as seen from the standard deviations. In zero enrichments, the expected value is 0 for all parameters (¹⁷δ, ¹⁸δ, ¹⁷Δ and δ(O₂/Ar)). For 50 measurements, ¹⁷δ and ¹⁸δ were found to be -0.006±0.018 ‰ and -0.023±0.020 ‰ respectively, which resulted in a ¹⁷Δ excess of 6±20 ppm. The difference for δ(O₂/Ar) was 0.01±0.12 ‰.

For the second test it was prepared the collection manifold in the line in such a way that the Valco valve was in CW position (so that ports 1 and 2 in the VALCO were connected, see Figure 2.2), hence the gas would go straight from the inlet to the collection manifold. The
results of 13 samples are shown in Table 2.2, row 2. The difference between these results and the O$_2$-Ar zero enrichment were 0.002 ‰ for $^{17}\delta$, 0.010 for $^{18}\delta$ and -0.31 ‰ for $\delta$(O$_2$/Ar). All these results show enrichment in the heavier isotopes and molecules, which is positive for $^{17}\delta$ and $^{18}\delta$ and negative for $\delta$(O$_2$/Ar). The direction of the fractionation points to a mass dependant fractionation. This means that the collection of the samples does fractionate but all samples and the dry air standard are affected in the same way. This reflects in $^{17}\Delta$ which does not change much, only 4 ppm which is within the standard deviation of the measurements of ±20 ppm for zero enrichment and ±9 ppm for this experiment. Also the standard deviation of each of the measurements (0.010 for $^{17}\delta$ and 0.021 for $^{18}\delta$) is within the standard deviation of the zero enrichment tests (0.018 for $^{17}\delta$ and 0.020 for $^{18}\delta$).

In the third experiment to test for possible fractionation a gas mixture of O$_2$-Ar was passed through the line and compared by IRMS against an unprocessed O$_2$-Ar mixture. The results are presented in Table 2.2, row 3. The results show that $^{17}\delta$ and $^{18}\delta$ are increased after passing through the line with an increase of 0.014 ‰ for $^{17}\delta$ and 0.040 ‰ for $^{18}\delta$ calculated as the difference of the O$_2$-Ar through the line minus the zero enrichment. On the other hand Barkan and Luz (2005) obtained less than 0.003 ‰ for both isotopes, in a similar experiment. Even though the difference here is larger than that of Barkan and Luz (2005), this small isotopic fractionation affects standards and samples in the same way and the effect cancels out for relative difference. The difference between the $^{17}\Delta$ of the processed and unprocessed sample indicates that the gas going through the line has a 6 ppm lower value. Such a small difference is irrelevant when compared with the standard deviation of the measurement of 13 ppm.

For $\delta$(O$_2$/Ar) it was observed a decrease of the O$_2$/Ar ratio of 2 ‰ which agree well with the reported elemental changes of Barkan and Luz of 3 ‰ (2005). The changes in the elemental ratios are so small that their effect can be neglected.

Finally it was tested for drift in the O$_2$-Ar extraction line. This was done on consecutive measurements of dry air between 6$^{th}$ and 21$^{st}$ of May 2011. The results for this test are shown in Table 2.2 row 4. Variability of $^{17}\delta$, $^{18}\delta$ and $\delta$(O$_2$/Ar) was within the variability of the O$_2$-Ar mixture going through the line.
Table 2.2: Results of the analysis by IRMS presented in rows in the following order: O₂-Ar zero enrichment; O₂-Ar frozen into the stainless steel tubes of the collection manifold; O₂-Ar through the line; and dry air through the line. Results are presented as the $\delta^{17}$O/$\delta^{16}$O anomaly ($\delta^{17}$); $\delta^{18}$O/$\delta^{16}$O anomaly ($\delta^{18}$); the relative difference in between the sample and standard in the O₂/Ar ratios as $\delta(O_2/Ar)$; and the $\delta^{17}$O excess ($\delta^{17}$) as defined in chapter 1 and n is the number of measurements

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{17}$ (%)</th>
<th>$\delta^{18}$ (%)</th>
<th>$\delta(O_2/Ar)$ (%)</th>
<th>$\delta^{17}$ (ppm)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂-Ar zero enrichment</td>
<td>-0.006 ± 0.018</td>
<td>-0.023 ± 0.020</td>
<td>0.01 ± 0.12</td>
<td>6 ± 20</td>
<td>50</td>
</tr>
<tr>
<td>O₂-Ar frozen into SS</td>
<td>-0.004 ± 0.010</td>
<td>-0.013 ± 0.021</td>
<td>-0.30 ± 0.16</td>
<td>2 ± 9</td>
<td>13</td>
</tr>
<tr>
<td>O₂-Ar through the line</td>
<td>0.008 ± 0.024</td>
<td>0.017 ± 0.047</td>
<td>-0.21 ± 0.23</td>
<td>0 ± 13</td>
<td>19</td>
</tr>
<tr>
<td>dry air through line</td>
<td>-0.471 ± 0.022</td>
<td>-0.864 ± 0.043</td>
<td>13.31 ± 0.13</td>
<td>-23 ± 15</td>
<td>21</td>
</tr>
</tbody>
</table>

2.3.5. Comparison with other laboratories

A common practice for comparisons between laboratories is to measure the isotopic composition of O₂ in air saturated samples. The procedure for preparation of this water was similar to that of Barkan and Luz (2003) and it was prepared as follows. Artificial sea water was prepared by adding NaCl salt to a glass jar of 4 l in a water bath at 15.5 °C. The water was poisoned with HgCl₂ and was allowed to equilibrate for at least 24 h with the atmospheric air in the lab by stirring and bubbling it constantly. Equilibrated water was siphoned into sampling bottles and processed following the normal procedure described in this chapter after a period of equilibration of at least 24 h. The average ± standard deviation results for 12 samples were 0.354±0.063 ‰ for $\delta^{17}$, 0.653±0.122 ‰ for $\delta^{18}$, giving $\delta^{17}$ = 15±5 ppm and with $\delta(O_2/Ar)$ = 0.20±0.18 ‰. The values here are referenced versus air which is the reference used in these studies. The $\delta(O_2/Ar)$ agrees well with what it was expected to fractionate if we compare the tests of O₂-Ar through the line with the zero enrichment which gives a difference of 0.22%. Moreover the standard deviation obtained for the equilibrated water 0.18% is comparable to those of the other tests (Table 2.2).

Despite the standard deviation of the measurements for $\delta^{17}$ (0.063 ‰) and $\delta^{18}$ (0.122 ‰) being greater than for the rest of the tests, the values for $\delta^{17}$ (0.354 ‰) and $\delta^{18}$ (0.653 ‰) were within the limits of the reported values in the literature (Table 2.3) for which the lowest reported values were of Reuer et al. (2007) of 0.340 ‰ and 0.642 ‰ and the highest by Luz and Barkan of 0.424 ‰ and 0.811 ‰ for $\delta^{17}$ and $\delta^{18}$ respectively.

Following from Luz and Barkan (2009) who reported a positive temperature dependence of $\Delta^{17}$ here is presented this relationship for all the reported data. Their
relationship was of \( \Delta = 0.606 + 1.7763 \theta \), which is very similar to the one reported here of \( \Delta = 0.539 + 2.5724 \theta \). The distance of our measurements (15±5 ppm) to that of this relationship is of 4 ppm, which is within the standard deviation of our measurements. If we include only the relationship given by Luz and Barkan (2009) our measurements would be separated by only 3 ppm. This shows that despite the bigger uncertainties, our data agree well with other studies.

Table 2.3: Measurements of equilibrated waters for several studies. This table is modified version of table 1 compiled by Kaiser (2011b) adding the equilibrated measurements from this study. Reported are the source of the data, how the equilibrated waters were prepared, \( \theta \) as the temperature of preparation, \( n \) the number of measurements, \( ^{17}O/^{16}O \) anomaly (\( ^{17}\delta \)), \( ^{18}O/^{16}O \) anomaly (\( ^{18}\delta \)) and the derived \( ^{17}\Delta \). A dash – means a value that has not been reported.
Figure 2.6: Relationship of temperature (θ) and $\Delta^{13}C$ of values reported in the literature shown in Table 3. The labels on the points represent the authors of the data with Luz and Barkan (2000) (LB’00); Juranek and Quay (2005) (JQ’05); Sarma et al. (2003) (Sa’03); Sarma et al. (2006b) (Sa’06); Reuer et al. (2007) (Re’07); Luz and Barkan (2009) (LB’09); and this study (GG’12).

\[ y = 0.539x + 2.5724 \]

\[ R^2 = 0.5705 \]
Chapter 3. Methods
3.1. Introduction

In this chapter is presented how core and ancillary data was collected, analysed and calibrated for the calculation of mixed-layer net community production ($N$) and gross production ($G$) from dissolved $O_2$ species in two different locations in Atlantic surface waters. $N$ is estimated from continuous measurements of $O_2$/Ar in the underway seawater supply (USW) with a membrane inlet mass spectrometer (MIMS) and $G$ from discrete samples collected in bottles and analysed later by isotope ratio mass spectrometry (IRMS).

First, are described the sampling campaigns, then the USW and the conductivity–temperature–depth (CTD) sensor on a rosette frame with Niskin bottles attached for sample collection. Next, is explained the sample collection and analysis of $O_2$ by the Winkler method and by an optode, followed by the sampling of $O_2$/Ar ratios by the MIMS as well as discrete sampling of seawater in evacuated bottles for analysis of $O_2$ isotopologues and $O_2$/Ar dissolved in the water. Finally, is described how it was evaluated the gas transfer coefficient $k$ for use in the budget calculations of $N$ and $G$.

3.2. Sampling campaigns

The North Atlantic Bloom experiment 2008 (NAB’08) took place south of Iceland in spring 2008. The data for this thesis was collected on the main process cruise on board R/V *Knorr*, which had cruise number KN193-03 and departed from Reykjavik on 1 May 2008 and returned to Reykjavik on 21 May. The region of study was centred on 26° W 61° N (Figure 3.1). The aim of NAB’08 was to study the evolution of the North Atlantic Spring Bloom in four dimensions (time, latitude, longitude and depth) using gliders and floats for the duration of the spring bloom. The cruise objectives were to calibrate and compare the productivity data derived from the autonomous platforms with other productivity measurement approaches ($^{14}$C incubation, oxygen isotopes).

The second cruise was cruise JC032 on board RRS *James Cook* along 24° S. The ship departed from Montevideo (Uruguay) on 7 March and arrived in Walvis Bay (Namibia) on 21 April 2009. This cruise was part of the CLIVAR (Climate Variability and Predictability) repeat hydrography program, which aims to repeat sections done during and since the WOCE (World Ocean Circulation Experiment) programme. The specific aim of the cruise was to assess the present-day circulation by calculating heat, freshwater and carbon transport across 24° S in comparison with previous cruises in the area like CLIVAR transects A9 at 19° S (1991), A10 at...
30° S (1993, 2003) and 24° S (R/V Oceanus, 1983). The JC032 cruise was divided into 4 transects, with three sections across the Brazil Current and a fourth section that crossed the South Atlantic at 24° S (Figure 3.2). Samples for this research project were collected mainly from the USW with complementary measurements at CTD stations.

![Figure 3.1: Map showing the location of the study. Blue colours represent depths in m as indicated by the colourbar. The black colouring represents depths above sea level, in this case Iceland. The red line represents the cruise track.](image1)

![Figure 3.2: Map of the cruise track (black line) and the stations (red dots) occupied during cruise JC032, black lines indicate isobaths.](image2)
3.3. Underway sea water supply

The underway sea water supply (USW) provided seawater to the laboratories directly from the bow of the ship.

On R/V Knorr the intake was at 3.7 m below sea level. Sensors for measuring temperature and conductivity were located at the entrance of this intake (SBE). This temperature sensor was calibrated against the CTD sensor (Sea-Bird SBE 911plus) on the rosette frame. This was done with salinity as well.

For RRS James Cook the intake was located 5.5 m below the water level. A sensor in the intake of the USW continuously recorded sea surface temperature (SST, FSI OTM Remote Temperature 1370), and downstream from this, in the water sampling room, two conductivity sensors recorded salinity (FSI OCM conductivity 1333 and SBE45 Micro TSG 0231). SST was calibrated against 2 CTD temperature sensors. The salinity was calibrated against the CTD sensor and discrete samples taken every 4 h and analysed using a salinometer (Guildline Autosal 8400B, serial no. 68426).

Sampling the USW

The $O_2$ concentration, $c(O_2)$, in the surface waters was measured continuously by an optode, which was calibrated against discrete $O_2$ samples analysed by the Winkler method with the purpose of calculating the saturation state of the surface waters, expressed as saturation anomaly $\Delta(O_2)$. Also the oxygen-to-argon ($O_2$/Ar) ratio was determined continuously in the water from the USW with a MIMS. MIMS data were calibrated with equilibrated water standards.

Several meteorological sensors, including a barometer for atmospheric pressure and an anemometer to measure wind speed, were located on the foremast of both ships at 16 m (R/V Knorr) and 20 m (RRS James Cook) above sea level.
Table 3.1: Types and number of samples collected during KN193-03 and JC032. Also included is the purpose of their collection. $c(O_2)$ in the table stands for the concentration of $O_2$, $c(Ar)$ the concentration of $Ar$, $\Delta(O_2/Ar)$ is the biological saturation anomaly of $O_2$ and $^{17}\delta$ and $^{18}\delta$ are the relative $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotope ratio differences between dissolved $O_2$ and atmospheric $O_2$.

<table>
<thead>
<tr>
<th></th>
<th>USW no. samples</th>
<th>purpose</th>
<th>CTD no. samples</th>
<th>purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winkler</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KN193-03</td>
<td>61 replicates</td>
<td>$c(O_2)$, calibrate optode</td>
<td>131</td>
<td>calibration CTD sensor</td>
</tr>
<tr>
<td>JC032</td>
<td>149 replicates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$ Optode</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KN193-03</td>
<td>continuous</td>
<td>$c(O_2)$, calculate $c(Ar)$ MIMS</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>JC032</td>
<td></td>
<td></td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>MIMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KN193-03</td>
<td>continuous</td>
<td>$\delta(O_2/Ar)$</td>
<td>----</td>
<td>depth profile</td>
</tr>
<tr>
<td>JC032</td>
<td></td>
<td></td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Evacuated bottles</td>
<td></td>
<td>$\delta(O_2/Ar), {^{17}\delta}, {^{18}\delta}$</td>
<td>51</td>
<td>$O_2/Ar, {^{17}\delta}, {^{18}\delta}$</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>57</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4. CTD

The CTD SBE 911 on R/V Knorr was mounted in a rosette with 24 Niskin bottles of 10 l. It had 2 temperature (SBE3T) and 2 salinity sensors (SBE4C). It also had $O_2$ and turbidity sensors, as well as an altimeter and fluorometer. A total of 131 samples, not including replicates, were collected for analysis of $c(O_2)$ by Winkler titration in order to calibrate floats and gliders for the NAB’08 mission. In addition, 51 samples were collected from Niskin bottles for analysis of $O_2$ isotopologues.

The CTD on the RRS James Cook was a Seabird 911 plus and it was mounted on a rosette with four 20 l Niskin bottles and twenty 10 l Niskin bottles. It comprised a pressure sensor, 2 temperature sensors, 2 conductivity sensors, and had the following additional sensors: an oxygen sensor, a fluorometer, a transmissometer and a backscatter sensor. Samples were collected from the Niskin bottles to measure the salinity, and concentrations of $O_2$, inorganic nutrients (nitrate, phosphate and silicate), CFCs (chlorofluorocarbons), $SF_6$ (sulphur hexafluoride), inorganic carbon parameters (alkalinity and dissolved inorganic carbon, DIC), total chlorophyll and $O_2/Ar$ ratios.

On JC032 a total of 17 evacuated headspace bottles (2 full depth profiles and 4 surface only stations) were taken for subsequent analysis of the $O_2/Ar$ ratio and $O_2$ isotopologues ratios using an Isotope Ratio Mass Spectrometer (IRMS) at the University of East Anglia (UEA).
3.5. Sample collection and analysis

3.5.1. Winkler analysis

Samples for Winkler O₂ analysis were collected in conical glass flasks (Pyrex, Mexico) with a nominal volume of 125 cm³. The accurate volumes at 20 °C were determined gravimetrically before the cruise. The flasks were filled directly from the USW. All the tubing used for filling the samples was soaked for at least 24 h to avoid the formation of bubbles in the tubing. Every bottle was filled by putting the tubing at the bottom of the bottle and by letting it overflow for three bottle volumes. This procedure avoids any contamination with bubbles. Once all the samples had been collected, the reagents were added and the bottles were kept for future analysis. Oxygen analyses were carried out using automated Winkler titrators. The titration unit for R/V Knorr was equipped with a photometric end point detector (custom built); the one for RRS James Cook was based on an amperometric end point detector (Winkler Ω-Metrohm, 794 DMS Titrino).

Following Dickson (1995), blanks and standards were analysed during each run. Both blanks and standards were prepared with the reference material potassium iodate (KIO₃) and were used for the calculation of the c(O₂) present in the samples. Blanks are used to account for possible interference with the reagents by other species present in the water. The standards are analysed to check for drift in the standard solution of thiosulphate (Na₂S₂O₃). The formulas used for the calculation are presented here:

\[
m_{\text{sample}} = \left[ V_{\text{bottle}} (1 + 10^{-5} (T_{\text{fix}}/°C - 20)) / -2 \text{ cm}^3 \right] \rho_{\text{sw}} \tag{3.1}
\]

\[
n(O_2) = \frac{1.5 (V - V_{\text{blank}}) V_{\text{KIO}} c(\text{KIO}_3)}{V_{\text{std}} - V_{\text{blank}}} \tag{3.2}
\]

\[
c(O_2) = \frac{-7.6 \times 10^{-8} \text{ mol}}{m_{\text{sample}}} \tag{3.3}
\]

The mass of the sample \(m_{\text{sample}}\) is calculated from the bottle volume at 20 °C \(V_{\text{bottle}}\) while taking into account the change in volume due to temperature (Culberson, 1991) with \(T_{\text{fix}}\) being the Celsius temperature during sample fixation and \(\rho_{\text{sw}}\) the density of sea water at in situ temperature. The amount of O₂, \(n(O_2)\), is calculated from the volume of thiosulphate used to
titrate the sample ($V$), the volume of the blank ($V_{\text{blank}}$), the volume of the standard ($V_{\text{std}}$), the volume of KIO$_3$ added in the preparation of the standards ($V_{\text{KIO3}}$) and the concentration of the reference material, $c$(KIO$_3$). The concentration of O$_2$, $c$(O$_2$), is calculated from $n$(O$_2$), while taking into account the O$_2$ content of the reagents ($7.6 \times 10^{-8}$ mol) used for titrating the samples (sodium hydroxide NaOH, sodium iodide NaI, manganese chloride MnCl$_2$).

Calibrations for each specific cruise are given below.

For KN193-03 blanks were prepared during two titration calibration sessions with distilled water. Because both values were statistically identical 0.0033±0.0019 ml (average ± standard deviation) and 0.0019±0.0013 ml, Table 3.2-a), and the same reagents were used in both sessions, an average of 0.0026 ml was used for the whole cruise. Standards to measure the thiosulphate concentration were measured in 11 sessions (Table 3.2-b). These standards were prepared with a reference material KIO$_3$. This solution was prepared gravimetrically at UEA using a potassium iodate certified reference material (Fluka, 60386) before the cruise.

As seen in Table 3.2-b initially it appeared that the thiosulphate decreased in concentration over time. This is the opposite of what is expected. So once on land the cruise KIO$_3$ solution was compared against a set of fresh new KIO$_3$ solutions. It appeared that the cruise KIO$_3$ had increased in strength by 0.24% since before the cruise. This explained the apparent decrease in the thiosulphate during the cruise. Assuming a linear concentration change over time, the concentration of thiosulphate was stable (Table 3.2-b column 6). Therefore, it was decided to use an average of the thiosulphate concentrations for the calculation of the O$_2$ concentration of the samples.

Table 3.2-a: Blanks prepared for KN193-03 with information on when they were prepared, the number of replicates prepared (# rep), the average value of the replicates, the standard deviation (st dev) and the standard error (st error, expressed as the st dev over the average in %).

<table>
<thead>
<tr>
<th>Date</th>
<th># rep</th>
<th>V blank(cm$^{-3}$)</th>
<th>average</th>
<th>stdev</th>
<th>st error</th>
</tr>
</thead>
<tbody>
<tr>
<td>02/05/2008</td>
<td>4</td>
<td>0.0033</td>
<td>0.0019</td>
<td>57%</td>
<td></td>
</tr>
<tr>
<td>07/05/2008</td>
<td>6</td>
<td>0.0019</td>
<td>0.0013</td>
<td>68%</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2-b: Standards prepared for KN193-03 with information on when they were prepared, the number of replicates prepared (# rep), the average concentration of the $c(Na_2S_2O_3)$ given by the replicates, the standard deviation (st dev), the standard error (st error, expressed as the st dev over the average) and the $c(Na_2S_2O_3)$ corrected for a change in concentration of KIO$_3$ (corr KIO$_3$, see text for details).

<table>
<thead>
<tr>
<th>date</th>
<th># rep</th>
<th>average $c(Na_2S_2O_3)$/mol l$^{-1}$</th>
<th>st dev</th>
<th>st error</th>
<th>corr KIO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>01/05/2008</td>
<td>6</td>
<td>0.2017</td>
<td>2.52E-04</td>
<td>0.12%</td>
<td>0.2017</td>
</tr>
<tr>
<td>01/05/2008</td>
<td>4</td>
<td>0.2018</td>
<td>1.81E-04</td>
<td>0.09%</td>
<td>0.2018</td>
</tr>
<tr>
<td>03/05/2008</td>
<td>5</td>
<td>0.2017</td>
<td>3.20E-04</td>
<td>0.16%</td>
<td>0.2017</td>
</tr>
<tr>
<td>05/05/2008</td>
<td>4</td>
<td>0.2017</td>
<td>2.83E-04</td>
<td>0.14%</td>
<td>0.2018</td>
</tr>
<tr>
<td>07/05/2008</td>
<td>6</td>
<td>0.2016</td>
<td>4.77E-04</td>
<td>0.24%</td>
<td>0.2018</td>
</tr>
<tr>
<td>13/05/2008</td>
<td>3</td>
<td>0.2011</td>
<td>8.40E-05</td>
<td>0.04%</td>
<td>0.2014</td>
</tr>
<tr>
<td>14/05/2008</td>
<td>5</td>
<td>0.2015</td>
<td>1.17E-04</td>
<td>0.06%</td>
<td>0.2019</td>
</tr>
<tr>
<td>16/05/2008</td>
<td>4</td>
<td>0.2013</td>
<td>2.59E-04</td>
<td>0.13%</td>
<td>0.2017</td>
</tr>
<tr>
<td>17/05/2008</td>
<td>4</td>
<td>0.2013</td>
<td>1.48E-04</td>
<td>0.07%</td>
<td>0.2018</td>
</tr>
<tr>
<td>18/05/2008</td>
<td>6</td>
<td>0.2014</td>
<td>1.68E-04</td>
<td>0.08%</td>
<td>0.2019</td>
</tr>
<tr>
<td>19/05/2008</td>
<td>4</td>
<td>0.2014</td>
<td>3.37E-04</td>
<td>0.17%</td>
<td>0.2019</td>
</tr>
</tbody>
</table>

The reason for the apparent increase in the KIO$_3$ concentration is unclear, but is suspected that one of the ports on the lid of the KIO$_3$ reservoir was not sealed, which would have led to evaporation.

For JC032, analyses of blanks and standard calibrations were carried out jointly with the O$_2$/nutrients team from the National Oceanography Centre, Southampton (NOC). On the cruise a total of 149 USW water samples (329 analyses including replicates, usually duplicates and sometimes triplicates) were measured for their O$_2$ content in a total of 10 sessions. For each calibration one set of blanks and one set of standards were prepared following Dickson (1995). Because there was a shortage of KIO$_3$, all standards were prepared with 5 cm$^3$ instead of 10 cm$^3$ (except for the first session). Table 3.3 lists all the sessions with their blanks and standards. Two different solutions of thiosulphate were used: thio1 from the beginning of the cruise to 26 March and thio2 from then onwards. Session 9 calibration data was not used because the calibration result was inconsistent and had a high standard deviation (see Figure 3.3); probably due to errors during preparation of the calibration mixtures. For the calibration of the Winkler samples, the average of all the blanks from the cruise was used. For the standards, the average thiosulphate concentration for 3 different sets of sessions was used: the first set includes the first 2 sessions with the first thiosulphate solution, the second set only includes session 3 with the new thiosulphate solution that had a slightly higher concentration...
than the third set, and finally the third set that included the rest of the titration sessions during which the thiosulphate concentration were roughly constant (Figure 3.3).

Regarding the precision of the measurements, the average of the standard deviations of all the replicates collected during this cruise is 0.1 μmol kg\(^{-1}\) which is smaller than the recommendation of 0.5 μmol kg\(^{-1}\) from the JGOFS protocol (Dickson and Goyet, 1994).

Table 3.3: Standard and blank sessions for JC032. In the columns are represented the number of replicates (# rep), the average volume for the blanks and the average thiosulphate concentration c(Na\(_2\)(S\(_2\)O\(_3\))) with their standard deviation (st dev) and standard error (st error, which is the standard deviation divided by the average).

<table>
<thead>
<tr>
<th>thio session</th>
<th># rep</th>
<th>average (ml)</th>
<th>std dev</th>
<th>std error</th>
<th># rep</th>
<th>c(Na(_2)(S(_2)O(_3)))/mol l(^{-1})</th>
<th>average</th>
<th>std dev</th>
<th>std error</th>
</tr>
</thead>
<tbody>
<tr>
<td>thio 1</td>
<td>1</td>
<td>5</td>
<td>0.0029</td>
<td>0.0009</td>
<td>5</td>
<td>0.1981</td>
<td>0.0006</td>
<td>0.30%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5</td>
<td>0.0030</td>
<td>0.0014</td>
<td>5</td>
<td>0.1985</td>
<td>0.0006</td>
<td>0.30%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5</td>
<td>0.0022</td>
<td>0.0022</td>
<td>6</td>
<td>0.1994</td>
<td>0.0005</td>
<td>0.26%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5</td>
<td>0.0005</td>
<td>0.0010</td>
<td>6</td>
<td>0.2000</td>
<td>0.0007</td>
<td>0.33%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5</td>
<td>0.0015</td>
<td>0.0005</td>
<td>5</td>
<td>0.2002</td>
<td>0.0005</td>
<td>0.23%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5</td>
<td>0.0019</td>
<td>0.0016</td>
<td>5</td>
<td>0.2006</td>
<td>0.0005</td>
<td>0.26%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>6</td>
<td>0.0017</td>
<td>0.0004</td>
<td>5</td>
<td>0.2001</td>
<td>0.0004</td>
<td>0.20%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>5</td>
<td>0.0015</td>
<td>0.0006</td>
<td>7</td>
<td>0.2005</td>
<td>0.0002</td>
<td>0.12%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>5</td>
<td>0.0021</td>
<td>0.0002</td>
<td>5</td>
<td>0.1980</td>
<td>0.0017</td>
<td>0.84%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5</td>
<td>0.0019</td>
<td>0.0007</td>
<td>5</td>
<td>0.2002</td>
<td>0.0002</td>
<td>0.12%</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.3: Concentration of sodium thiosulphate during cruise JC032 with error bars showing the standard deviation.
3.5.2. Optode

The aim of measuring with an optode was to have continuous measurements of the concentration of \( \text{O}_2 \) in surface waters. Combination of these \( \text{O}_2 \) concentrations with the \( \text{O}_2/\text{Ar} \) data from the MIMS allows calculation of the \( \text{Ar} \) concentrations and therefore of the physical \( \text{O}_2 \) super-saturation.

**Technical description of optode measurements**

The optode (Aanderaa Data Instruments, Norway, model 3835) is an instrument capable of measuring the concentration of oxygen in water. The principle behind the measurement is the special property of a substance called luminophore that changes its fluorescence and its decay time depending on the presence and concentration of certain materials. In the case of the optode the luminophore is a platinum porphyrine complex embedded in a foil that reacts with the \( \text{O}_2 \) gas molecule. This phenomenon is called dynamic luminescence quenching Tengberg *et al.* (2006).

The platinum porphyrine is mounted on a PVC layer in a chamber inside the optode. To protect the luminophore it is separated from the outside with a gas permeable coating that eliminates possible contact with direct sunlight and separates it from the surroundings.

The optode is composed of different parts: The sensing foil, which contains the platinum porphyrine, and two LEDs. A blue LED is used for the excitation of the luminophore and the red LED is used for corrections if needed. Between the two sits a photodiode detector.

The gas present in the water passes through the coating to the chamber by diffusion. At the same time the porphyrine is excited with an intermittent pulse of the blue LED. The \( \text{O}_2 \) molecules constantly interact with the surface of the porphyrine and produce a change in the fluorescence (numerically described by the Stern-Volmer effect). The fluorescence is measured by the photodiode and saved to the computer as the \( \text{D}_{\text{phase}} \), which is the change of the response time due to the presence of \( \text{O}_2 \).

Since the change of intensity in the fluorescence can drift over time, it is preferable to use the change of the fluorescence decay time, which decreases at higher concentrations of \( \text{O}_2 \) (Tengberg *et al.*, 2006).

The optode was mounted inside a bucket where tubing from the USW was seated at the bottom such that the renewal of water would be from bottom to top. The optode made continuous measurements every 10 s. The optode measurements were extracted at the times at which discrete samples for Winkler analyses were taken, such that they could be compared to identify outliers and calibrate the optode.
Analysis, calibration and comparison of different calibration methods

For KN193-03 a total of 61 USW samples for \( \text{O}_2 \) were collected (141 including replicates), the average standard deviation of the replicates was of 0.31 \( \mu \text{mol kg}^{-1} \).

Calibration of the USW was done by comparing the D\_phase of the discrete samples collected from the USW to the D\_phase of the optode (Figure 3.4). The discrete samples concentration was converted to an equivalent D\_phase by mathematically inverting the polynomial given as sensing foil calibration by the manufacturer. From this, a calibration function was derived by linear regression and used to correct the raw D\_phase readings of the optode. The corrected D\_phase readings were then converted back to \( c(\text{O}_2) \) using again the polynomial given by the manufacturer. The average ± standard deviation of the residuals was 0.00±0.91 \( \mu \text{mol kg}^{-1} \).

![Figure 3.4: Calibration curve for \( \text{O}_2 \) optode against the discrete Winkler solved D\_Phase. Black crosses depict the data used of the calibration in red are the data considered to be outliers.](image)

To calibrate the CTD \( \text{O}_2 \) sensor a direct comparison of the sensor measurement with discrete Winkler measurements was carried out.

The data were calibrated with 3 different sets of calibration. The first set ran from the beginning of the cruise until day 125 (I), the second set included day 125 to 135 (II) and the third would be from day 135 until the end of the cruise (III). Sets I and III were calculated as a
simple linear regression of \(c(O_2)\) measured by the CTD sensor vs. the \(c(O_2)\) measured by discrete Winkler samples. For set II, a second-degree polynomial was used for calibration. It depended on \(c(O_2)\) measured by the CTD and year-day. The standard deviation of the all the residuals from the three calibrations is 0.65 \(\mu\)mol kg\(^{-1}\). The relationships are presented in Table 3.4.

Table 3.4: Calibration equations for the \(O_2\) data from the CTD. \(c(O_2)\) is the calibrated concentration of \(O_2\), YD represents the year-day and \(c(O_2)\)\(_{\text{CTD}}\) represents the \(c(O_2)\) measured by the CTD sensor. All Oxygen concentrations are in \(\mu\)mol kg\(^{-1}\).

<table>
<thead>
<tr>
<th>yearday</th>
<th>equation</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I start-125</td>
<td>(c(O_2) = 1.02 \times c(O_2)_{\text{CTD}} + 7.46)</td>
<td>0.9992</td>
</tr>
<tr>
<td>II 125-135</td>
<td>(c(O_2) = 1.06 \times c(O_2)_{\text{CTD}} - 0.07 \times \text{YD}^2 + 19.54 \times \text{YD} - 1304.06)</td>
<td>0.9978</td>
</tr>
<tr>
<td>III 135-end</td>
<td>(c(O_2) = 1.07 \times c(O_2)_{\text{CTD}} - 1.22)</td>
<td>0.9966</td>
</tr>
</tbody>
</table>

For JC032 three different methods were compared for the calibration of the optode data.

The first method employed a “D\_phase inversion method” where the Winkler concentrations for the USW samples were transformed to D\_phase values by the equations given by the manufacturer Aanderaa. These manufacturer equations are expressed in equations 3.4 and 3.5, where \(a_0, a_1, a_2, a_3, b_{x0}, b_{x1}, b_{x2}, b_{x3}, b_{x4}\) are constants given by the manufacturer and shown in Table 3.5, \(T\) is the temperature in °C as measured by the optode and \(P\) is the D\_phase.

\[
c(O_2) = a_0 + a_1P + a_2P^2 + a_3P^3 + a_4P^4 \tag{3.4}
\]

\[
a_x = b_{x0} + b_{x1}T + b_{x2}T^2 + b_{x3}T^3 \tag{3.5}
\]

Table 3.5: Values for the coefficients in equation 3.5 where \(x\) is substituted for 0, 1, 2, 3 and 4.

<table>
<thead>
<tr>
<th>(b_{00})</th>
<th>(4945.29)</th>
<th>(b_{10})</th>
<th>(-269.898)</th>
<th>(b_{20})</th>
<th>(5.976379)</th>
<th>(b_{30})</th>
<th>(-0.06181859)</th>
<th>(b_{40})</th>
<th>(0.000245035)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b_{01})</td>
<td>(-167.764)</td>
<td>(b_{11})</td>
<td>(8.31507)</td>
<td>(b_{21})</td>
<td>(-0.167971)</td>
<td>(b_{31})</td>
<td>(0.001602029)</td>
<td>(b_{41})</td>
<td>(-5.90218E-06)</td>
</tr>
<tr>
<td>(b_{02})</td>
<td>(3.41751)</td>
<td>(b_{12})</td>
<td>(-0.174439)</td>
<td>(b_{22})</td>
<td>(3.75245E-03)</td>
<td>(b_{32})</td>
<td>(-3.91116E-05)</td>
<td>(b_{42})</td>
<td>(1.59999E-07)</td>
</tr>
<tr>
<td>(b_{03})</td>
<td>(-3.07691E-02)</td>
<td>(b_{13})</td>
<td>(1.628069E-03)</td>
<td>(b_{23})</td>
<td>(-3.6796E-05)</td>
<td>(b_{33})</td>
<td>(4.027959E-07)</td>
<td>(b_{43})</td>
<td>(-1.71557E-09)</td>
</tr>
</tbody>
</table>
The Winkler $D_{\text{phase}}$ was regressed linearly versus the $D_{\text{phase}}$ measured by the optode in order to obtain a calibration function. The residuals calculated with the calibration function are shown in Table 3.6.

The second method was based on the Stern-Volmer equation that describes the phenomenon of dynamic luminescence quenching. In this case, $c(O_2)$ measured by the optode would be calculated from the $D_{\text{phase}}$ as in equations 3.6, 3.7, 3.8 and 3.9 and then compared with the Winkler measurements.

\[
c(O_2) = \frac{[P_0 / P_c] - 1}{K_{sv}} \tag{3.6}
\]
\[
P_0 = 1 + c_1 T \tag{3.7}
\]
\[
P_c = c_2 + c_3 P \tag{3.8}
\]
\[
K_{sv} = c_4 + c_5 T + c_6 T^2 \tag{3.9}
\]

Where: $P_0/P_c$ is the ratio of the phase shift in the absence of $O_2$ ($P_0$) and the phase shift in the presence of $O_2$ ($P_c$), $P$ is the $D_{\text{phase}}$, $T$ the temperature in °C and $K_{sv}$ is the Stern-Volmer constant.

The values for the constants $c_1$ to $c_6$ were obtained by a non-linear parameter estimation (or unconstrained nonlinear optimisation), which finds the minimum of a scalar function of several variables, starting at an initial estimate. The initial values given to the coefficients from $c_1$ to $c_6$ were 0.017, 0, 0, 0.003, 0 and 0. The obtained best fitting set of coefficients from $c_1$ to $c_6$ are: -6.43 x 10^{-4}, -5.34 x 10^{-3}, 1.41 x 10^{-2}, 1.67 x 10^{-3}, 8.15 x 10^{-5} and 9.35 x 10^{-7}.

In the third method a multivariate polynomial dependent on temperature and the $D_{\text{phase}}$ from the optode is fitted to the concentrations of $O_2$ measured by Winkler titration Uchida et al. (2008). The polynomial was:

\[
c(O_2) = d_0 + d_1 T + d_2 T^2 + d_3 T^3 + d_4 P + d_5 P^2 + d_6 TP \tag{3.10}
\]

Where $P$ expresses the $D_{\text{phase}}$, $T$ the temperature (in °C) and the coefficients $d_0$ to $d_6$ (±standard error) are 11033 ±1566, -181.77 ±13.85, 1.3481 ±0.1096, -0.010488 ±0.001722, -503.04 ±84.18, 5.9982 ±1.1240 and 3.8344 ±0.3969. These coefficients were determined by least squares.
The residuals for each of the methods, calculated as the expected value minus the measured value, are compared in Table 3.6.

Table 3.6: Comparison of the different methods for calibrating the optode data with Winkler analysis (std dev is the standard deviation and $r^2$ the coefficient of determination) for JC032.

<table>
<thead>
<tr>
<th>Method</th>
<th>std dev (μmol kg$^{-1}$)</th>
<th>$r^2$</th>
<th># data</th>
<th>outliers removed number of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Aanderaa all</td>
<td>0.99</td>
<td>0.943</td>
<td>218*</td>
<td>0%</td>
</tr>
<tr>
<td>1 Aanderaa ± 3 stdev</td>
<td>0.82</td>
<td>0.950</td>
<td>207</td>
<td>5%</td>
</tr>
<tr>
<td>1 Aanderaa ± 2 stdev</td>
<td>0.47</td>
<td>0.988</td>
<td>170</td>
<td>22%</td>
</tr>
<tr>
<td>2 Stern-Volmer equation all</td>
<td>1.68</td>
<td>----</td>
<td>218</td>
<td>0%</td>
</tr>
<tr>
<td>2 Stern-Volmer equation ±3stdev</td>
<td>1.51</td>
<td>----</td>
<td>215</td>
<td>1%</td>
</tr>
<tr>
<td>2 Stern-Volmer equation ±2stdev</td>
<td>0.5</td>
<td>----</td>
<td>181</td>
<td>17%</td>
</tr>
<tr>
<td>3 Multivariate polynomial all</td>
<td>0.99</td>
<td>0.962</td>
<td>218</td>
<td>0%</td>
</tr>
<tr>
<td>3 Multivariate polynomial ± 3stdev</td>
<td>0.69</td>
<td>0.965</td>
<td>208</td>
<td>5%</td>
</tr>
<tr>
<td>3 Multivariate polynomial ± 2stdev</td>
<td>0.48</td>
<td>0.987</td>
<td>181</td>
<td>17%</td>
</tr>
</tbody>
</table>

* The initial number of data is more than the number of 149 samples and less than the number of analyses including replicates (329). This is because replicates, which were collected in periods of high variability (this were identified when even the optode signal varied by more than 0.6 μmol kg$^{-1}$ for those replicates) were considered independent.

The best fit of the data appears when we remove the outliers (distance from the regression line >2 standard deviations ($\sigma$) in all of the three methods, but a high proportion of data is lost (at least 17 %). The 3σ criterion shows an almost equally good fit and 5% or less of the data is removed. The 3σ criterion gives different standard deviations for each method, namely 1.51 μmol kg$^{-1}$ for the Stern-Volmer fit, 0.82 μmol kg$^{-1}$ for the manufacturer calibration and 0.69 μmol kg$^{-1}$ for the multivariate analysis. The multivariate analysis with the 3σ criterion is used for calibration of the optode.

### 3.5.3. Continuous MIMS data

The O$_2$/Ar ratio has been measured continuously with a membrane inlet mass spectrometer as described by Kaiser et al. (2005). Similar instrument have been deployed by several other authors (Kana et al. (1994), Tortell (2005a), Guéguen and Tortell (2008), Nemcek et al. (2008) and Stanley et al. (2010)). The MIMS consists of a quadrupole mass spectrometer and a membrane module to extract the gases dissolved in water.
3.5.3.1. Set up of the MIMS in the shipboard laboratory

The MIMS is mounted next to a sink. It consists of 2 different parts: The first part extracts the gases from the water and comprises a water-pump, tubing and a semi-permeable membrane. The second part is a quadrupole mass spectrometer (QMS), which detects different gas species. Gases dissolved in seawater arrive through a semi-permeable membrane that allows gases through but not water (Figure 3.5).

The pump in the first part of the MIMS (Figure 3.5) brings the water to the semi-permeable membrane where another pump in the QMS creates a gradient so gases travel from the water, through the semi-permeable membrane, to the QMS. In the QMS the gas is ionized, accelerated and analysed through four parallel rods arranged as a quadrupole. One pair of opposite rods have the same direct current voltage applied while the potential difference between the other two rods oscillates and extracts ions depending on their mass-to-charge (m/z) ratios. This is why the instrument is capable of detecting several gases nearly simultaneously (every 10 s) by just changing the frequency. It was measured m/z 32 (O₂) and 40 (Ar), as well as others with m/z 28 (N₂), 29 (¹⁴N¹⁵N), 44 (CO₂) and 18 (H₂O).

![Figure 3.5: Set up of the MIMS on the cruises. USW stands for underway sea water, SW for sea water, 4p-2w four port-2 way valve and QMS is the quadrupole mass spectrometer.](image)

For both cruises the overall setup was very similar. The only differences were: First, the membrane enclosure was different on each cruise: for KN193-03 a cartridge (Membrana Liquicel) was used and for JC032 a custom built membrane box, which contained a tubular
Teflon AF membrane (Random Technologies), was used. Second, as the data was collected during a bloom, a filter in the intake to the MIMS on KN193-03 was fitted, so the system would not become clogged up with plankton cells.

3.5.3.2. Analysis and calibration for KN193-03

No equilibrated waters were prepared for this cruise due to technical problems and the data could not be calibrated against the discrete O₂/Ar samples because it is likely that the cartridge use for this cruise kept clogging and was of slow response so there was not linear relationship between the continuous O₂/Ar and the discrete samples (Figure 3.6).

![Figure 3.6: Comparison of the Δ(O₂/Ar) as measured by the IRMS versus the MIMS](image)

3.5.3.3. Analysis and calibration for JC032

To test for drift in the mass spectrometer m/z 28, 32, and 40 were measured in a range of 5 different mass-to-charge ratios (m/z) separated by 0.03 (see Table 3.7). This is done to check whether the strongest signal (therefore the most accurate) is always centred on the same m/z.
Table 3.7: The mass to charge ratios m/z and the corresponding molecules measured on the MIMS on JC032.

<table>
<thead>
<tr>
<th>molecule</th>
<th>m/z</th>
<th>molecule</th>
<th>m/z</th>
<th>molecule</th>
<th>m/z</th>
<th>molecule</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>31.97</td>
<td>Ar</td>
<td>39.94</td>
<td>N2</td>
<td>28.00</td>
<td>H2O</td>
<td>18.00</td>
</tr>
<tr>
<td>32.00</td>
<td>39.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.03</td>
<td>40.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.06</td>
<td>40.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.09</td>
<td>40.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.12</td>
<td>40.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.14</td>
<td>40.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This was not the case; it was proved by looking at the maximum signal for these 5 m/z ratios by fitting a quadratic relationship of the m/z versus signal response (voltage) and taking the m/z ratio at which the maximum value of this fit occurred. When this maximum was plotted over time, a trend was discovered showing drift in the MIMS and a shift of the strongest signal to heavier mass to charge ratios over time (Figure 3.7). The data used were these maximum intensities.

Figure 3.7: Maximum signal in the mass to charge ratios as identified by a quadratic fit to the 5 collected masses for O2 and Ar along JC032.

A second test for the stability consists of measuring “standard” air-saturated seawater twice daily, the equilibrated water inFigure 3.8. This standard is seawater that has been allowed to equilibrate with atmospheric air pump from the tallest point in the ship’s roof to
the lab by a KNF pump) for at least 12 h at a constant temperature of 15 °C (controlled by a water bath, Thermo Neslab RTE-10), such that the saturation of oxygen and argon for each of these standard solutions is constant throughout the cruise.

To run this water to the MIMS (Figure 4), first the valve to the waste is opened to remove bubbles in the tubing and then the four-port two-position valve is switched, thus allowing the equilibrated water to run to the quadrupole mass spectrometer. The valve is kept like this for 6 minutes, sufficiently long to get a stable signal for the O₂/Ar ratio of the standard. After this period the valve is switched back to resume USW sampling.

Figure 3.8 shows the O₂/Ar ratio of these equilibrated waters and it is obvious that there is a positive correlation between time and the O₂/Ar signal.

![Figure 3.8: O₂/Ar ratio of the runs with equilibrated waters at 15 °C for JC032.](image)

This drift was quantified with a linear regression which was then applied to all the data. The correction has the equation:

\[
(O_2/Ar)_{EW} = (O_2/Ar)_{raw-EW} - (0.016 \times YD + 21.672)
\]  

(3.11)

Where the value for the O₂/Ar ratio for the equilibrated water is \((O_2/Ar)_{EW}\), YD is the days since “31/12/2008” and \((O_2/Ar)_{raw-EW}\) is the ratio of O₂/Ar when the equilibrated water was run. This regression had a coefficient of determination, \(r^2\) of 0.915 \((n = 60)\). The short term
reproducibility of the O$_2$/Ar ratios determined by the MIMS, expressed as a relative error (standard deviation over the average), and was 0.14 \% over a period of 45 min.

With this fit the values of the continuous measurements on the MIMS were corrected following this equation:

$$
\Delta(O_2/Ar) = \frac{(O_2/Ar)_{raw}}{(O_2/Ar)_{EW}} \frac{(O_2/Ar)_{sat-EW}}{(O_2/Ar)_{sat-in situ}} - 1
$$

(3.12)

Where (O$_2$/Ar)$_{raw}$ is the value for the continuous measurements, (O$_2$/Ar)$_{sat-EW}$ is the saturation concentration ratio of the gases O$_2$ (Garcia and Gordon, 1992) and Ar (Hamme and Emerson, 2004) calculated for equilibrated seawater 15°C and a salinity of 35 and the (O$_2$/Ar)$_{sat-in situ}$ is the saturation concentration calculated for in situ temperature and salinity.

### 3.5.4. Analysis of the O$_2$/Ar ratio and the O$_2$ isotope content by IRMS

#### 3.5.4.1. Sampling

The samples for the O$_2$/Ar ratio and O$_2$ isotopes were taken in evacuated bottles (Figure 3.9) for analysis by IRMS. Sampling was carried out at least once a day and in most cases twice a day in order to get as much geographical coverage as possible. On KN193-03 a total of 39 samples were taken from the USW and 51 from CTD stations. For JC032 a total of 74 samples were taken with 57 samples from the USW and 17 bottles from CTD stations. The sampling was always done at the same time of the day around 05:00 and 17:00 GMT.

Samples for the O$_2$/Ar ratio and O$_2$ isotopes were collected in 400 cm$^3$ flasks, which had previously been evacuated and poisoned with 7.6 mg HgCl$_2$ (100 μl of a saturated solution of mercuric chloride). Thanks to the T-neck design of the flasks, it is possible to first fill only their necks and let the water overflow. Once the sample has been overflowing for a few seconds the tap is opened and seawater is allowed to enter at the bottom of the flask. Once the bottle is approximately half full, then the tap is closed and the bottle is sealed with water on its neck to minimize exchange with O$_2$ from the air. These bottles were stored for later analysis at UEA.
In order to avoid deterioration samples from KN193-3 were extracted 7 months after collection in glass sealed tubes, which were eventually analysed 4 years after collection. For JC032 samples were extracted and analysed 2 years after collection.

![An evacuated bottle with a sample.](image)

**Figure 3.9: An evacuated bottle with a sample.**

### 3.5.4.2. Isotope ratio mass spectrometry measurements

Once on land, the headspace of the bottles containing the samples was run through an extraction line for the removal of H₂O vapour, CO₂ and N₂, as these might interfere with the analysis of the O₂ isotopologues in the (IRMS) MAT 252. This extraction line, built in the stable isotope laboratory at the University of East Anglia, was based on that of Barkan and Luz (2003) and is described in Chapter 2.

Samples were run through the extraction line in sets of 5 to 6 samples and one aliquot of 2ml of reference gas per day. The reference gas was always drawn from the same tank of dry air. It was collected at UEA by Andrew Manning’s lab and dried to reach a water vapour mole fraction of less than 2 x 10⁻⁶. The purpose of this dry air was to calibrate the samples and to check how reproducible the line was. All the samples and the reference gas were collected on a collection manifold, which consisted of stainless steel fingers each protected by a valve (Swagelok 6LVV-DPS4-C) with 0.050 g of molecular sieve 5Å pellets in them. Each stainless steel finger was preconditioned for 2 min at 300 °C in order to remove all gases adsorbed to the molecular sieve pellets.

Once the gas was in the collection finger, it was analysed by IRMS the next day. For each measurement a sample and a “working reference” (O₂-Ar mixture of 4.7% of Ar in O₂ from BOC) were put in the bellows on the sample and the standard side, respectively. The bellows are two flexible receptacles where the gas is kept for analysis. They are connected to the source by independent capillaries. The flow on these capillaries is regulated by the
pressure on the bellows, thus allowing changing the flow at which the sample or the standard enters the source (Figure 3.10), such that the same signal intensity can be achieved on the collectors shown in the figure below.

Once the bellows are filled with the sample and working reference gas the procedure is as follows: first the gas from standard enters the source where it is ionized and accelerated to form the ion beam that goes to the flight tube. In the flight tube the magnet deviates the ions according to their mass to charge ratio. Ions are collected on the ion detectors where their intensity is recorded during the chosen set time (integration time). This procedure repeats itself with the sample. These cycles of a standard and sample run are separated by a set time (idle time), so the signal of one gas is not mixed with the other. This procedure is repeated for 30 cycles. Measurements from the mass spectrometer for the oxygen (O) isotopes are the average of these 30 cycles and are calculated as follows:
Where * stands for 17 and 18 for the $^{17}$O$^{16}$O and $^{18}$O$^{16}$O isotopes of O$_2$. $^{16}$O in the formula stands for O$_2$ formed by the two light isotopes $^{16}$O and ref refers to the reference.

IRMS measurements were performed according to the following daily routine: First, zero enrichment is used to test the performance of the mass spectrometer, which is done by putting the working reference gas with the O$_2$-Ar mixture in both bellows (standard and sample side). Then the dry air standard plus the 6 samples all prepared the previous day in the extraction line follow (see Chapter 2).

Each gas sample was run for 3 blocks of measurements containing 30 cycles each. The integration time was 16 s, the idle time 5 s and the measurement intensity 3.5 V with a $3 \times 10^8$ $\Omega$ feedback resistor. At the beginning of each block a peak centre for the standard was performed at $m/z$ 32 in order to find the maximum intensity for the signal. Then, both bellows (standard and sample side) were adjusted to 3.5 V in the major cup. Interfering masses were measured at the end of the third block and were run in the $m/z$ order of: 32, 40 and 28. Mass to charge ratio 32 (O$_2$) and 40 (Ar) were measured in the same major collector, whereas the $m/z$ 28 ($N_2$) was measured in a minor detector capable to detect 1/300 times smaller concentrations than in major detectors.

### 3.5.4.3. Calculation of O$_2$/Ar ratios by IRMS

O$_2$ and Ar were measured as $m/z$ 32 and 40 respectively for a sample and the working reference (work_ref). The initial $\delta_{\text{sample/work_ref}}$ (O$_2$/Ar) was calculated as:

$$
\delta_{\text{sample/work_ref}} (O_2/Ar) = \left( \frac{^{32}/^{40}}{^{32}/^{40}} \right)_{\text{sample/working ref}} - 1 \tag{3.15}
$$

Dry air is used as a standard for the O$_2$/Ar and isotopologues analysis. Dry air is used as the standard, because the O$_2$/Ar ratio in the atmosphere is well known and is constant.
(Glueckauf, 1951), while at the same time dry air is an internationally accepted reference for O\textsubscript{2} isotopologues (Barkan and Luz (2003); Wieser (2007)). The use of atmospheric O\textsubscript{2} is preferred to Vienna Standard Mean Ocean Water (VSMOW), firstly because the isotope ratios of dissolved O\textsubscript{2} samples are closer to atmospheric O\textsubscript{2} than to VSMOW and secondly because atmospheric air is readily available. Any processes fractionating atmospheric O\textsubscript{2} are likely to occur on timescales greater than 1000 years and are therefore negligible for the purposes of this study.

Then the $\delta_{\text{sample/dry air}}$ (O\textsubscript{2}/Ar) is:

$$\delta_{\text{sample/dry air}} (O_2/Ar) = \frac{\delta_{\text{sample/工作中}} (O_2/Ar) - \delta_{\text{dry air}} (O_2/Ar)}{1 + \delta_{\text{dry air}} (O_2/Ar)} - 1 \quad (3.16)$$

To obtain the final O\textsubscript{2}/Ar of the sample it is necessary to correct for the distribution of gases between the gas phase and the water phase. This correction factor $Q$ described by Luz et al. (2002) was applied as per the following equation:

$$\delta_{\text{sample}} (O_2/Ar) = Q \delta_{\text{sample/dry air}} (O_2/Ar) \quad (3.17)$$

$$Q = \frac{1 + \alpha(O_2) \frac{V_{\text{gas}}}{V_{\text{water}}}}{1 + \alpha(Ar) \frac{V_{\text{gas}}}{V_{\text{water}}} \quad (3.18)}$$

Where $\alpha^{(16}O_2)$ is the Ostwald solubility and $V_{\text{gas}}$ and $V_{\text{water}}$ are the volume of the headspace and water. The supersaturation of O\textsubscript{2} as in equation 3.16 can be calculated from $\delta(O_2/Ar)_{\text{sample}}$.

### 3.5.4.4. O\textsubscript{2} Isotopologues by IRMS

The IRMS values for $^{17}O^{16}O$ and $^{18}O^{16}O$ were obtained from the m/z measurements 33 and 34, respectively, from two of the minor cups. The software from the IRMS gave the $^{33}\delta$ and $^{34}\delta$ which are assumed to be exactly the same as $^{17}\delta$ and $^{18}\delta$ since the conversion correction is very small (Kaiser and Röckmann, 2008).
The $\delta(N_2/O_2)$ correction was evaluated by combining the $O_2$-Ar working reference with 7 different gas mixtures containing different amounts of $N_2$.

![Calibration curves for $^{17}\delta$ and $^{18}\delta$ versus $\delta(N_2/O_2)$.

Just as in previous studies (Castro-Morales, 2010) I found a relationship between $\delta(N_2/O_2)$ and $^{17}\delta$, but not with $^{18}\delta$ (Figure 3.11), probably due to interaction in the ion source of the $N_2$ with the $O_2$. Therefore only $^{17}\delta$ was corrected for this effect. No correction was applied to $^{18}\delta$, as there is no significant dependence on $N_2/O_2$. A linear fit was calculated and the $^{17}\delta$ values were corrected with the equation below.

$$^{17}\delta_{N_2}^{corr} = ^{17}\delta_{meas} - (0.0050 \delta(N_2/O_2) + 0.0003) \quad (3.19)$$

The measurements were also referenced against the dry air standard in a similar way as done for $\delta(O_2/Ar)$. To calculate the $\delta$ referenced to dry air we use this equation:
Where $i$ stands for 17 or 18 depending on which oxygen isotope is being calculated, $\text{^{17}O}$ or $\text{^{18}O}$.

Finally, $\delta^{18}$ was corrected for the fractionation between the gas and water phase in the storage bottle. Such fractionation mostly affects $\text{^{18}O}$ and to a lesser extent $\text{^{17}O}$. The correction was typically:

\[
\delta^* = \delta_{\text{sample/dry air}} \cdot \frac{Q}{1 + \alpha(\text{^{18}O}) \frac{V_{\text{gas}}}{V_{\text{water}}}} \tag{3.21}
\]

\[
Q = \frac{1}{1 + \alpha(\text{^{16}O}_2) \frac{V_{\text{gas}}}{V_{\text{water}}}} \tag{3.22}
\]

Where $^*$ stands for 17 or 18 referring to $\text{^{17}O}$ or $\text{^{18}O}$. The Ostwald solubility coefficient for oxygen is $\alpha(\text{^{16}O}_2)$. The $\alpha(\text{^{18}O} - \text{^{16}O})$ was calculated as follows:

\[
\alpha(\text{^{18}O}) = \alpha(\text{^{16}O}_2)(1 + \delta_{\text{sat}}) \tag{3.23}
\]

The headspace correction was 0.002% for $\delta^{18}$ and 0.001% for $\delta^{17}$.

### 3.6. Gas exchange parameterizations and wind speed

The gas transfer coefficient is crucial for the estimation of the net community production and gross oxygen production ($N$ and $G$). There are several parameterizations of $k$, e.g. Liss and Merlivat (1986), Wanninkhof (1992), Nightingale et al. (2000) and Sweeney (2007). In this study we decided to use the parameterization by Nightingale et al. (2000), because it is based on real measurements and it is between the estimates of Wanninkhof and Liss and Merlivat. The $k$ defined by Nightingale et al. is:
\[ k_i = \frac{24}{100}(0.333 \ U_{10} + 0.222 \ U_{10}^2) \left( \frac{S_e}{600} \right)^{-0.5} \]  

(3.24)

Where \( k_i \) is the instantaneous gas transfer coefficient (m d\(^{-1}\)), \( U_{10} \) is the wind speed at 10 m height (m s\(^{-1}\)), and \( S_e \) the (dimensionless) Schmidt number for O\(_2\) defined by Wanninkhof (1992) for salinity 35 and temperatures \( T \) between 0 °C and 30 °C:

\[ S_e = 1953.4 - 128.00 \ T + 3.9918 \ T^2 - 0.050091 \ T^3 \]  

(3.25)

In this work I use the weighting technique of \( k \) according to the history of the wind speed for up to 60 days prior to sampling \( k_w \) (Reuer et al., 2007). The weighting factors are calculated from the mixed layer depth \( z_{mix} \) as well as the gas transfer velocities. \( z_{mix} \) was calculated from CTD profiles on JC032 and defined as the depth where the change in the density relative to the surface value (≈ 10 m) was greater than 0.125 kg l\(^{-1}\) compared to that of surface waters (average of 0-10 m). This calculation assumes that \( z_{mix} \) has not changed during the weighting period. Arbitrarily, \( \omega \) is set to 1.

\[ k_w = \frac{\sum_{i=1}^{60} k_i \omega_i}{\sum_{i=1}^{60} \omega_i} \]  

(3.26)

\[ \omega_i = \omega_{i-1} (1 - f_{i-1}) \]  

(3.27)

\[ f_i = k_i \frac{0.25 \ d}{z_{mix}} \]  

(3.28)

Where, \( f_i \) is the fraction of the mixed layer ventilated throughout 6 h (0.25 days) and \( \omega_i \) is the weighting factor. \( k \) is a major source of uncertainty in the calculation of \( F_{bio} \).

Leaving the uncertainty due to the different parameterizations of \( k \) aside, a 15 % relative error in the wind speed causes an error of up to 30 % in \( N \), because of the quadratic term in the Nightingale et al. (2000) parameterisation. The exact error depends on the value of the wind speed. Therefore it was identified which wind dataset best matched the measured ship winds.
Wind speeds were measured on the *RRS James Cook* with a Gill Windsonic anemometer located in the foremast of at 19.9 m above sea level. These wind speeds were corrected to a height of 10 m using the wind profile power law expressed here (Peterson and Hennessey, 1978):

\[
\frac{U_{10}}{U_m} = \left( \frac{z_{10}}{z_m} \right)^\alpha
\]  

(3.29)

Where \(U_{10}\) is the wind speed in m s\(^{-1}\) at 10 m (\(z_{10}\)) and \(U_m\) is the wind speed in m s\(^{-1}\) at the measurement location of 19.9 m (\(z_m\)).

The wind products were from the National Centre for Environmental Prediction (NCEP, Kalnay *et al*. 1996), the European Centre for Medium-Range Weather Forecasts (ECMWF, 2009) and the Cross-Calibrated Multi-Platform Ocean Surface Wind Velocity Product (CCMP, Atlas *et al*. 2009). A comparison of the different wind products and the wind speed measured on the ship was carried out, as shown in Figure 3.12. All the wind products had a time resolution of 6 h, but varied spatially from 1° latitude by 1° longitude for NCEP and ECMWF to 0.25° latitude by 0.25° longitude for CCMP. The root mean square difference (RMSD) between the shipboard wind speed and the three products was calculated. I got a difference of 1.89 m s\(^{-1}\) for NCEP, 1.14 m s\(^{-1}\) for ECMWF and 1.00 m s\(^{-1}\) for CCMP. Thus, CCMP was closest to the shipboard wind in this region of the ocean.

![Figure 3.12: Wind speed (in m s\(^{-1}\)) at 10 m above sea level during cruise JC032 from the shipboard sensor and from wind products from NCEP, ECMWF and CCMP.](image)
Chapter 4. Oxygen production in the subtropical South Atlantic from $O_2$/Ar ratios and $O_2$ isotopologues
4.1. Introduction

The South Atlantic gyre (SATL) is a vast, undersampled region covering 25% of the
Atlantic Ocean. It is known as an oligotrophic region where nutrient inputs are small;
therefore, biological production rates are low (Longhurst, 2007). However, despite its low
production rates, the size of the gyre makes this area relevant for global carbon budgets, and it
is important to know whether the metabolic balance represents a net carbon sink or source to
the atmosphere.

Earlier studies of the metabolic balance in the SATL include Atlantic Meridional Transect
(AMT) cruises (Gist et al., 2009; González et al., 2002; Serret et al., 2006). These studies have
examined the metabolic state of the gyre in vitro by using bottle incubations of oxygen (O₂).
This method can produce biased results due to changes in the phytoplankton community
composition during bottle enclosure, e.g. a reduction in autotrophs during the incubation time
(Calvo-Díaz et al., 2011; Fernández et al., 2003), an increase in heterotrophs (Calvo-Díaz et al.,
2011) or the exclusion of grazers (Bender et al., 1999).

Using this method, González et al. (2002) found that the gyre was net heterotrophic
(community respiration greater than production), based on the data average for austral
autumn and spring of the same year (May and October 1997). However, their measurements
were made at the western edge of the gyre and it is not clear whether they can represent the
whole of the gyre. In contrast to González et al. (2002), Serret et al. (2002), using the same
techniques, found that the central region of the gyre was net autotrophic in spring. More
recently, Gist et al. (2009) found that the SATL was in balance in spring and net heterotrophic
in autumn (average of three spring and autumn cruises each).

An alternative method to measure the metabolic balance consists of measuring the O₂/Ar
ratio, e.g. with a membrane inlet mass spectrometer (Kaiser, 2005). This enables continuous
measurements of net oxygen production in the mixed layer along a ship transect (see
chapter 1).

Biological gross production by autotrophs can also be measured by bottle incubations,
e.g. based on ¹⁴C-labelled bicarbonate uptake rates or changes in O₂ concentration in
dark/light experiments. Here, are used in situ measurements of the isotopic composition of
dissolved O₂ in the mixed layer to estimate biological gross O₂ production (see chapter 1).
4.2. Methods

For this study, the South Atlantic was crossed on board of RSS *James Cook* cruise JC032 in early austral autumn of 2009, departing from Montevideo (Uruguay) 7th March and arriving to Walvis Bay (Namibia) on the 21st April (Figure 4.1). Samples from the mixed layer were analysed for their $O_2$/Ar and $O_2$ isotopologue ratios. The results were used for the calculation of net community ($N$) and gross oxygen production ($G$), respectively.

![Figure 4.1: Map showing the location of the cruise-track (black line) and CTD stations (red dots).](image)

The cruise JC032 was composed of three sections across the Brazil current at 37° S, 25° S and 24° S (8th to 20th March 2009) and a main section along 24° S (21st March to 20th April 2009), starting from the coast of Brazil at 40° W and ending in Africa at 12° E.

$O_2$/Ar ratios and oxygen concentrations, $c(O_2)$, were measured continuously using MIMS and an $O_2$ optode in the underway sea water supply (USW) every 10 s, corresponding to about 50 m spatial resolution. Discrete samples were collected from the USW to measure the
isotopic composition of dissolved O$_2$ for the quantification of the gross oxygen production (G). Additionally, $F_u/F_m$ ratios in the USW were measured using fast rate repetition fluorescence (FRRF). O$_2$ concentrations in the USW were measured using Winkler titrations (Dickson, 1995) at regular intervals, as described in the cruise report (King et al., 2010), and used to calibrated the optode measurements.

A more detailed description of the individual measured parameters is given in the following sections. Some ancillary measurements and calibrations were done by different groups: A team led by Sinhué Torres (National Oceanography Centre, Southampton, NOCS) performed additional dissolved O$_2$ as well as nutrient measurements in Niskin samples from rosette hydrocasts. Mark Moore (NOCS) measured chlorophyll a concentrations, nitrogen isotope ratios ($\delta^{15}$N) in particulate organic nitrogen and, at selected stations, nitrogen fixation rates (using $^{15}$N-labelled N$_2$). Lorna McLean and Ben Moat (NOCS) calibrated the underway and CTD temperature and salinity measurements, see the cruise report for details (King et al., 2010).

### 4.2.1. Temperature and salinity measurements

A FSI remote temperature module FSI OTM (serial number 1370) was used for sea surface temperature ($\theta_b$) measurements near the USW intake. It was calibrated using CTD temperatures from 118 stations. Sea surface salinity ($S_b$) was measured using an FSI OCM conductivity sensor (serial number 1333) located in the rosette sampling room of the RRS James Cook. Salinity measurements were calibrated against 242 discrete salinity samples measured with a Guildline Autosal 8400B (serial number 68426) and the surface salinity measurements done at 118 CTD stations.

### 4.2.2. Continuous measurements of O$_2$ in the surface waters

$c(O_2)$ was measured in the USW with an O$_2$ optode (Aanderaa, Norway; model 3835, serial number 329). The calibration procedure is detailed in Chapter 3. In brief, the O$_2$ signal of the sensor (DPhase) was compared with 218 (plus 111 replicates) discrete Winkler samples collected from the USW (Figure 4.2). To accomplish this, the Winkler O$_2$ concentrations were converted to equivalent DPhase values by inverting the optode-specific, temperature and concentration-dependent calibration function.

There were some periods with bubbles in the USW. These are identified by sudden changes of the order of 2-15 μmol kg$^{-1}$ in $c(O_2)$ over less than 1 min. They occurred during year-
day 69.5-71.5 and 99-105 and corresponded to periods when the ship speed was under 4.6 kn and wind speeds greater than 5 m/s. In contrast, the sudden increase of \(c(O_2)\) on year-day 75.5 is associated with a decrease in salinity and temperature most likely associated with a different water mass than the surrounding Brazil current. Excluding these bubble periods, repeatability of the optode measurements is high, with only 0.02% difference between samples over 30 min, calculated as the standard deviation divided by the mean.

![Image](image.png)

**Figure 4.2:** \(O_2\) concentrations, \(c(O_2)\) measured by the optode (black points) in the underway sea water (USW) versus time (year-day represents the days since year 2009 started, day 1= 1\textsuperscript{st} January). Red dots represent the discrete samples used to calibrate the optode. Turquoise dots represent \(O_2\) concentrations as measured from discrete surface Niskin samples. Panel a) shows the data from the Brazil current section only, while panel b) presents the data from the main section of the cruise at 24° S from west to east. Note that in panel b) the y-axis has been magnified to visualise the variability in \(c(O_2)\).

Because a disagreement between the \(\Delta(O_2)\) and \(\Delta(O_2/Ar)\) data with the \(\Delta(O_2/Ar)\) showing values always above saturation whereas \(\Delta(O_2)\) showed mostly undersaturation it was raised the alarm of a problem with the calibration in the \(c(O_2)\) measured by the Winkler
titration. To check the quality of the Winkler O$_2$ concentrations, Oliver Legge (UEA) compared them to previous cruises using the CARINA database and a Matlab tool-box available in the CDIAC website (http://cdiac.ornl.gov/oceans/2nd_QC_Tool) (Tanhua, 2010). JC032 data were compared to two cruises (CLIVAR A16S 2005 [CARINA record no. 49NZ20031106] and CLIVAR/Carbon A10 [33RO20050111]) that crossed the path of cruise JC032 in the Brazil current section at 44° E and at 25° E. Samples within a specific distance (222 km x 222 km; latitude x longitude) were selected, from depths greater than 1500 m to avoid any seasonal or interannual variations. c(O$_2$) for JC032 data was found to be 3% (±0.6%) lower than those of the previous two cruises. I therefore applied a correction of +3% to the Winkler O$_2$ data. This correction has already been taken into account in Figure 4.2. It brings the O$_2$ saturation anomalies, Δ(O$_2$), into much better agreement with the O$_2$/Ar saturation anomalies, Δ(O$_2$/Ar), see below.

Previous studies (Juranek et al., 2010) found evidence of O$_2$ consumption in USW lines. Therefore, I compared c(O$_2$) from the surface Niskin bottle with c(O$_2$) measured by the optode and the discrete Winkler samples taken from the USW, which were taken at the same time as the surface Niskin bottle was fired (Figure 4.3). The average difference between the oxygen concentration from the USW and the upper Niskin are negative, indicating a loss of O$_2$ in the USW pipes of the ship, probably due to respiration. For the Winkler bottles, the average depletion of O$_2$ was -0.9±0.9 μmol kg$^{-1}$, while the more complete optode dataset gave a depletion of -1.2±1.4 μmol kg$^{-1}$.

![Figure 4.3: Oxygen consumption in the USW pipes of the RSS James Cook calculated as c(O$_2$) measured in the USW minus c(O$_2$) measured in the surface bottle of the CTD (from 5 m depth). Crosses (x) were calculated from c(O$_2$) measured by the optode and black circles (●) measured by the Winkler titration.](image-url)
Using the calibrated and corrected O\textsubscript{2} concentrations from the optode, the O\textsubscript{2} saturation anomaly was calculated as:

\[
\Delta(O_2) = \frac{c(O_2) + \Delta c(O_2, R_p)}{c_{sat}(O_2)} - 1
\]  

(4.1)

where \(\Delta c(O_2, R_p) = 1.2 \text{ µmol kg}^{-1}\) corrects for respiration in USW pipes and \(c_{sat}(O_2)\) is the saturation concentration of O\textsubscript{2} at \textit{in situ} temperature, salinity and atmospheric pressure (corrected to sea level).

\textbf{4.2.3. Calculation of air-sea O\textsubscript{2} fluxes}

The air-sea flux of O\textsubscript{2}, \(F(O_2)\), was calculated as

\[
F(O_2) = \Delta(O_2) \cdot k_w \cdot c_{sat}(O_2)
\]  

(4.2)

where \(k_w\) is the gas transfer coefficient calculated following a similar procedure as Reuer \textit{et al.} (2007) and is described in Chapter 3. Essentially, the gas transfer coefficient is calculated as a weighted gas transfer coefficient that takes into account the historical wind speed of the area \((k_w)\). The wind-speed gas exchange parameterisation of Nightingale \textit{et al.} (2000) was used together with CCMP winds as explained in Chapter 3.

Mixed layer depths \((z_{mix})\) were calculated as the depth at which there was a change of density of 0.125 kg/m\textsuperscript{3} from a reference depth of 10 m.

\textbf{4.2.4. Calculation of diapycnal O\textsubscript{2} fluxes between mixed layer and thermocline}

The euphotic zone in the gyre was deeper than the mixed layer. This led to the formation of an O\textsubscript{2} maximum just below the mixed layer (Figure 4.4), with a flux of O\textsubscript{2} that depends on the O\textsubscript{2} concentration gradient. This flux of O\textsubscript{2} \((F_v(O_2))\) was estimated using:
where the oxygen concentration gradient over depth is $\Delta c(O_2)/\Delta z$ and $K_v$ is the vertical eddy diffusivity. As no direct measurements of $K_v$ were available the flux was calculated with $K_v = (1.7 \pm 0.2) \times 10^{-5}$ m$^2$ s$^{-1}$, the quantity measured by Ledwell et al. (1998) during a tracer release experiment in the North Atlantic Gyre.

This flux was calculated to estimate the leakage of signal from below the mixed layer.

4.2.5. Continuous measurements of $O_2/Ar$ ratios for determination of $N$

$O_2/Ar$ ratios in the surface waters were measured continuously with a membrane inlet mass spectrometer (MIMS). The MIMS was calibrated twice daily using equilibrated water; this procedure is explained in detail in Chapter 3. The calibrated data were used to calculate the biological saturation anomaly of $O_2$, $\Delta(O_2/Ar)$, which is:

$$\Delta(O_2/Ar) = R(O_2/Ar) / R_{sat}(O_2/Ar) - 1$$ (4.4)
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where $R(O_2/Ar)$ and $R_{sat}(O_2/Ar)$ are the ratios of the $O_2$ and $Ar$ concentrations, at in situ conditions and at air saturation, respectively.

$\Delta(O_2/Ar)$ was used to calculate the biological air-sea flux of $O_2$ to the atmosphere as

$$F_{bio}(O_2/Ar) = \Delta(O_2/Ar) k_w c_{sat}(O_2) \quad (4.5)$$

where $k_w$ is the weighted gas transfer coefficient, calculated using a weighted historical wind speed value for the previous 60 days of sampling.

Assuming only vertical diffusion of $O_2$ from the mixed layer to the waters below ($F_v$) and no horizontal exchange, net community production ($N$), would be calculated as:

$$N(O_2/Ar) = F_{bio}(O_2/Ar) - F_v \quad (4.6)$$

The $Ar$ saturation anomaly can be calculated from $\Delta(O_2)$ and $\Delta(O_2/Ar)$ to estimate the relevance of physical processes as:

$$\Delta(Ar) = \frac{\Delta(O_2) - \Delta(O_2/Ar)}{1 + \Delta(O_2/Ar)} \quad (4.7)$$

4.2.6. Gross oxygen production measured using $O_2$ isotopologues

Discrete samples from USW and selected CTD stations were taken to measure their isotopic content; 57 samples were collected along with 17 samples from the CTD at different depths. Samples were measured on land in the Stable Isotope Laboratory (SIL, UEA). The analysis of $^{17}\delta$ and $^{18}\delta$ is described in Chapter 3. $^{17}\delta$ and $^{18}\delta$ were used to calculate the ratio between gross $O_2$ production and the $O_2$ flux from the atmosphere ($g$) (Kaiser, 2011b):
Where $\Delta(O_2)$ is the saturation anomaly of $O_2$; $^{17}\epsilon$ and $^{18}\epsilon$ are the kinetic $^{17}O/^{16}O$ and $^{18}O/^{16}O$ fractionation during $O_2$ evasion from sea to air; $\gamma_R$ is the $^{17}\epsilon/^{18}\epsilon$ ratio of respiratory $^{17}O/^{16}O$ and $^{18}O/^{16}O$ fractionation; $^{17}\epsilon_i$ and $^{18}\epsilon_i$ are the kinetic $^{17}O/^{16}O$ and $^{18}O/^{16}O$ fractionation during $O_2$ invasion from sea to air; $^{17}\delta$ and $^{18}\delta$ relative $^{17}O/^{16}O$ and $^{18}O/^{16}O$ differences between measured $O_2$ and air $O_2$; and $^{17}\delta_p$ and $^{18}\delta_p$ relative $^{17}O/^{16}O$ and $^{18}O/^{16}O$ differences between photosynthetic $O_2$ and air $O_2$.

Gross oxygen production, $G$, was then calculated using:

$$G = g k_w c_{sat}(O_2)$$

(4.9)

where $g$ is calculated by Eq. 4.8; $k_w$ is the weighted gas transfer coefficient and $c_{sat}(O_2)$ is the saturation concentration of $O_2$ at in situ conditions.

**4.2.7. Fast Repetition Rate Fluorometer**

Variable fluorescence ($F_v/F_m$) was measured in the USW by Fast Repetition Rate Fluorometer (Chelsea Instruments Ltd.). $F_v/F_m$ measures the effective absorption of light by Photo System II (PSII), and it has been used as an indicator of light stress or nutrient limitation (Cassar et al., 2011; Huang et al., 2012). It is an indirect measurement of the efficiency with which light is used to fix carbon, with low values indicating low carbon fixation due to high stress by either lack of nutrients or light excess. For this study, we fed a FRRF instrument with a continuous flow of USW and recorded one $F_v/F_m$ value every 10 s. Only night-time data were used, as during the day PSII is saturated, which makes it impossible to discriminate between light and nutrient stress. For the discussion here only the minimum $F_v/F_m$ measured during a given night is retained.
4.2.8. Nitrogen-related measurements

Nitrate concentrations were used to calculate a nutrient limitation index \( z_{\text{lim}} \) following Behrenfeld et al. (2002):

\[
z_{\text{lim}} = z_{\text{NO}_3} - z_{\text{mix}}
\]  

(4.10)

where \( z_{\text{NO}_3} \) is the first depth at which the concentration of nitrate is above the detection limit (0.15 \( \mu \text{mol kg}^{-1} \)) and \( z_{\text{mix}} \) is the mixed layer depth. The higher \( z_{\text{lim}} \), the higher the nutrient stress.

Samples for \( \delta^{15}\text{N} \) analyses of particulate organic nitrogen were collected at 32 different locations from the USW and filtered and frozen for analysis (Mark Moore, NOCS). The nitrogen isotope ratio is used as a tracer of nitrogen sources. \( \delta^{15}\text{N} \) between 0 and 1 ‰ correspond to \( \text{N}_2 \) fixation, whereas higher values around 5 ‰ indicate nitrate-based production (Karl et al., 2002).

Depth profiles of nitrogen fixation rates were also measured by Mark Moore at 36 CTD stations. Samples were collected from the Niskin bottle into Nalgene polycarbonate bottles and sealed to avoid contamination with bubbles. The samples were then enriched with 3-4 ml of \( ^{15}\text{N}_2 \) gas and incubated on deck for 24 h, simulating “in situ” conditions. Afterwards, these samples were filtered and frozen for later analysis at NOCS.
4.3. Results

The results from the main section across the oligotrophic gyre are described first because the gyre was the focus of this study, followed by the sections across the Brazil current.

Results for the main section pertain to data collected between 37° W and 14° E, beginning on 20th March 2009, en route to the first station off the coast of Brazil. Data collected within this section were composed of two different physical-chemical regimes (explained below): a more homogenous part (hereafter, gyre section, 37° W to 8° E), and the part influenced by the Benguela current (hereafter Benguela section, 8° E to 14° E).

4.3.1. Temperature, salinity and oxygen concentration variations

Sea surface temperatures ranged from 16 °C to 28 °C (Figure 4.5a). Higher temperatures were found at the western edge of the gyre and decrease steadily at a rate of –0.14 °C per degree longitude towards the African coast where temperatures of 22 °C were reached at 8° E. From 8° E until the transect end at 14° E, in the Benguela section the temperatures varied sharply and decreased to a minimum of 16 °C. Salinity (Figure 4.5b) ranged from 34 to 37, with values decreasing steadily towards the African coast. Salinity also presented more pronounced changes close to Brazil, influenced by coastal processes.

The calibrated optode oxygen concentration $c(O_2)$ varied from 197 μmol kg$^{-1}$ to 258 μmol kg$^{-1}$ (Figure 4.5c). $c(O_2)$ in the gyre was of 209±7 μmol kg$^{-1}$, although it increased with proximity to the African coast at a rate of 0.55 μmol kg$^{-1}$ per degree longitude and reached a maximum of 227 μmol kg$^{-1}$ at 8° E. This rate of change corresponds to the observed rates of change of $θ_0$ and $S_0$. Between 8° E and 14° E, $c(O_2)$ varies more sharply and reaches values as high as 258 μmol kg$^{-1}$, which is probably associated with the Benguela upwelling. Bubbles appeared in the USW between 6° W and 5° E and, as explained in the methods, were present whenever the ship speed was under 4.6 kn and wind speed greater than 5 m/s.

The $O_2$ saturation anomaly (Figure 4.5d) shows a consistent supersaturation along the whole of the gyre with an average ± standard deviation value of 2.6±0.3 %. High values occur between 6° W to 5° E consistent with the observed $c(O_2)$ in that area. For the Benguela section, the $Δ(O_2)$ varies much more than in the gyre with values ranging from -5% to 10%, which are out of scale (Figure 4.5d), with an average ± standard deviation 3.3±2.1 %.

The air-sea $O_2$ flux $F(O_2)$ was positive everywhere, showing outgassing of $O_2$ to the atmosphere. The highest $F(O_2)$ values are associated with the bubble period, but if data from
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this period are ignored, $F(O_2)$ for the gyre section was $16 \pm 4 \text{ mmol m}^{-2} \text{ d}^{-1}$, whereas for the Benguela section the flux was $29 \pm 4 \text{ mmol m}^{-2} \text{ d}^{-1}$.

**Figure 4.5**: Five measured variables versus longitude travelled during the main section on cruise JC032. The white portion represents the gyre region, and the shaded grey region represents data from within the Benguela current (see text). Panels show: a) sea surface temperature; b) sea surface salinity; c) the calibrated and corrected optode oxygen concentration; d) $O_2$ saturation anomaly; and e) air-sea flux of $O_2$. 

![Figure 4.5 Image](image-url)
4.3.2. Mixed layer depth and nutrient limitation

Mean mixed layer depth ($z_{\text{mix}}$) along the gyre section was 47±12 m (range 10 m –70 m); within the Benguela section, it was 34±13 m. The nutrient limitation index ($z_{\text{lim}}$) varied little from -38° E to -15° E but decreased with the proximity to the African coast. The mean value was 48±36 m for the gyre and -20±14 m for the Benguela section. The data shows the gyre to be under nutrient stress, which decreases within the Benguela upwelling and eventually disappears.

![Figure 4.6](image)

**Figure 4.6**: a) Mixed layer depth calculated with a criterion difference of 0.125 kg m$^{-3}$ from a reference depth of 10 m versus longitude. b) Nutrient limitation index calculated as the difference between the first depth at which NO$_3^-$ concentrations are above detection limit minus mixed layer depth. Positive values indicate stations where the mixed layer is shallower than the nitracline, whereas negative values are stations where NO$_3^-$ is above detection limit and thus not nutrient limited. The vertical panel in grey shows the Benguela section, and the white represents the gyre section.
4.3.3. Net community production

\( N \) was calculated according to Eq. (4.6)

The biological oxygen saturation anomaly, \( \Delta(O_2/Ar) \), (Figure 4.7c) was positive across the gyre section, averaging 1.9±0.4 %. There was little variation overall, although the values decreased from west to east at a rate of -0.02 percentage points per degree longitude. Values for \( \Delta(O_2/Ar) \) in the Benguela section were higher (mean 2.5±1.9 %) but also more variable with values ranging from -7% at 13.3° E to 7% at 13.0° E. Overall, the \( O_2/Ar \) measurements had a standard deviation of 0.12 % over 1 min.

The weighted gas transfer coefficient (\( k_w \), Figure 4.7d) averaged 3.1±0.7 m d\(^{-1}\) (range 1.7 m d\(^{-1}\) to 4.5 m d\(^{-1}\)) in the gyre section and 4.3±0.1 m d\(^{-1}\) in the Benguela section.

\( F_v(O_2) \) (Figure 4.7a) is homogenous for the gyre section with an average value of 2.5±1.3 mmol m\(^{-2}\) d\(^{-1}\), corresponding to a diffusive flux of the \( O_2 \) into the mixed layer. For the Benguela section, \( F_v(O_2) \) averaged -1.3±3.1 mmol m\(^{-2}\) d\(^{-1}\), a negative value indicating a diffusion of \( O_2 \) out of the mixed layer.

\( N \) values (Figure 4.7e) ranged from 1 to 21 mmol m\(^{-2}\) d\(^{-1}\) for the gyre section with an average value of 10±3 mmol m\(^{-2}\) d\(^{-1}\), indicating a net flux of biological \( O_2 \) to the atmosphere. Variation in \( N \) was generated mainly by the variability in \( k_w \) (Figure 4.7-d) given the observed overall pattern, the peaks in both variables at 27° W, and the low variability in \( \Delta(O_2/Ar) \). Regression analyses showed that 37 % of the variability in \( N \) was caused by the variability in \( k_w \), whereas \( \Delta(O_2/Ar) \) accounts for 16 % of the variability in \( N \). An exception to this relationship between \( k_w \) and \( N \) occurs between 38° W and 34° W and for the Benguela section, where wind speeds are stable and \( \Delta(O_2/Ar) \) shows some variability. Moreover, from 5° W to the edge of the Benguela section, \( N \) is decoupled from wind speed; this is explained by \( \Delta(O_2/Ar) \) decreases from 5° W eastwards, which are partially compensating wind speed changes.

\( \Delta(Ar) \) is indicative of the physical saturation in \( O_2 \), this was calculated from the \( \Delta(O_2/Ar) \) and \( \Delta(O_2) \) (Figure 4.7-b). Its values are negative mainly on the western margin of the gyre section and gradually increased towards the Benguela section. Overall, mean \( \Delta(Ar) \) was 0.6±0.4 % for the gyre section (excluding the data with bubbles), and 1.2±0.7 % for the Benguela section.
Figure 4.7: a) Expected vertical diffusion flux into the mixed layer calculated using $K_v = 1.7 \times 10^{-5}$ m$^2$ s$^{-1}$, the black line separates positive values (indicating an entrainment of O$_2$ into the mixed layer) and negative fluxes (indicating a diffusion out of the mixed layer); b) Ar saturation anomaly; c) biological saturation anomaly; d) weighted gas transfer coefficient calculated similarly to Reuer et al. (2007); e) net community production, black points represent the raw data and the grey line represents the data smoothed with a moving average with a span of 3.33 h. Areas in white correspond to the gyre section and those in grey to the Benguela section.
4.3.4. Gross oxygen production

The ratio of gross oxygen production to gross oxygen uptake \((g, \text{Figure 4.8c})\) was higher in the gyre section (mean 0.28±0.13) than in the Benguela section 0.15±0.22. Gross oxygen production \((G, \text{Figure 4.8d})\) in the gyre section was 173±97 mmol m\(^{-2}\) d\(^{-1}\) (range: 13 mmol m\(^{-2}\) d\(^{-1}\) at 4.5° E to 381 mmol m\(^{-2}\) d\(^{-1}\) at 18.4° W). Average \(G\) in the Benguela section was 153±56 mmol m\(^{-2}\) d\(^{-1}\), (range: 101 mmol m\(^{-2}\) d\(^{-1}\) at 11.3° E to 229 mmol m\(^{-2}\) d\(^{-1}\) at 13.05° E). Unlike the variability observed in \(N\), which was due mostly to \(k_w\), 77% of variability in \(G\) was due to \(g\) and only 16% was due to the \(k_w\).

The entrainment calculated for the isotopes, \(F_v\) for \(O_2\) isotopologues, was calculated similarly as for the \(O_2/Ar\). Here I used samples with data in the mixed layer and below at two stations, one at 6° E and one at 11° E. Using \(K_v\) is \(1.7 \times 10^{-5}\) m\(^2\) s\(^{-1}\) and the gradient to the mixed layer the entrainment flux was calculated to be about 4% and 17% of \(G\) for stations at 6° E and 11° E, respectively. Given the similarity of the gradient of the c(O\(_2\)) across the gyre between 38° W and 10°E (see Figure 4.4), I assumed that the entrainment at 6°E was similar to that at the rest of the stations.

Surface concentrations of chlorophyll \(a\), \(c(chl \, a)\), (Figure 4.8a) varied very little along the gyre section. \(c(chl \, a)\) averaged 0.07±0.02 \(\mu g\) l\(^{-1}\), with the lowest values in the centre of the gyre around 12° W (0.04 \(\mu g\) l\(^{-1}\)) and higher values near the edges (0.11 \(\mu g\) l\(^{-1}\)). Values were higher in the Benguela section, where \(c(chl \, a)\) averaged 0.7±1.2 \(\mu g\) l\(^{-1}\), with the easternmost point reaching 2.8 \(\mu g\) l\(^{-1}\) at 13.7° E (out of scale, not shown on the graph).

The photosystem quantum efficiency \((F_v/F_m)\) varied from 0.26 to 0.42 (Figure 4.8-b) for the gyre section (mean 0.36±0.04) and 0.28 to 0.44 (mean 0.33±0.79) for the Benguela section.
Figure 4.8: Various variables versus longitude areas in white correspond to the gyre section and those in grey to the Benguela section. Panels show: a) chlorophyll α concentration; b) Photosystem II quantum efficiency (night-time minima, with the shaded gray area representing the standard deviation for the entire night; c) $g$ calculated with $\delta_{SMOW}$ as measured by Kaiser and Abe (2012) and using the exact equation of Kaiser (2011b) the black line representing the 4 point-moving average; d) gross oxygen production, with 4-point moving average.
4.3.5. Nitrogen sources (data from Mark Moore, NOCS)

Nitrogen fixation rates in the surface water (<10 m) of the gyre averaged ± standard deviation 2.1±8.2 nmol l^{-1} d^{-1}, with the highest rates (42.8 nmol l^{-1} d^{-1}) at the westernmost edge. N fixation rates decreased towards the east where values of 0.0 nmol l^{-1} d^{-1} were common. No surface data were collected for the Benguela section.

In the gyre section, the isotopic composition of particulate organic nitrogen, $\delta^{15}N$ (PON), averaged ± standard deviation 2.2±3.1 ‰ (Figure 4.9b). Values were lowest (as low as -2.1 ‰) between 40° W and 18° W and increased from 18° W until the end of the section, reaching a maximum of 8.6 ‰. The lower values in the western portion of the gyre and the higher nitrogen fixation rates (Figure 4.9a) suggest that the source of N is likely to be atmospheric $N_2$, with the processes converting atmospheric $N_2$ gas into organic matter through nitrogen fixation. Higher $\delta^{15}N$ PON values to the east suggest that the source of N to the ecosystem comes from below the mixed layer as $NO_3^-$, given the decreases in $z_{lim}$ (Figure 4.6b) and the low $N_2$ fixation rates in this area (Figure 4.9-a).

![Figure 4.9: a) $N_2$ fixation rates. Rates > 0.5 nmol l^{-1} d^{-1} were coloured dark red in order to be able to appreciate the small change in $N_2$ fixation in the middle of the gyre; b) Abundance of the $^{15}N$ isotope in the particulate organic nitrogen expressed as $\delta^{15}N$ and represented here versus atmospheric $N_2$.](image-url)
4.3.6. Brazil current

The region of the Brazil Current was subdivided into three areas, labelled from south to north as Brazil Current 1 (BC1), BC2, and BC3. In this region, the biological O\(_2\) supersaturation (\(\Delta(O_2/Ar)\)) ranged from 0.8 to 2.6 % (Figure 4.10.a). The highest values of \(\Delta(O_2/Ar)\) were found at the beginning of the cruise. Values reaching 2.4 % were recorded between 32° S and 29° S and were associated with the highest gas transfer coefficient (9 m d\(^{-1}\)) of this section and thus the highest estimates of \(N\) (50 mmol m\(^{-2}\) d\(^{-1}\)), which indicate net autotrophy. This is supported by the input of nutrients from below, as \(z_{\text{lim}}\) in BC1 had values below 0 (Figure 4.10.d).

Moving northwards from 32 to 28° S, while the \(\Delta(O_2/Ar)\) value remained high (1.8% to 2.4%), \(k_w\) was low (4 to 7 m d\(^{-1}\)) which leads to lower \(N\) values between 10 and 30 mmol m\(^{-2}\) d\(^{-1}\). Also, the nutrient limitation indicates a gradient from non-stressed areas in the BC1 to nutrient-limited areas in BC2.

The area of BC2 and up to 24° S shows the lowest \(\Delta(O_2/Ar)\) observed in this section. Here, \(\Delta(O_2/Ar)\) values ranging from 0.8 % to 1.8 %, together with low \(k_w\) (2 to 5 m d\(^{-1}\)), resulted in the lowest \(N\), with values between 5 to 10 mmol m\(^{-2}\) d\(^{-1}\). These low \(N\) values might be explained by the nutrient limitation observed for BC2.

In section (BC3), located between 40° W and 36° W, \(\Delta(O_2/Ar)\) ranged from 2 to 2.4 %, but because \(k_w\) was only 5 m d\(^{-1}\), \(N\) did not exceed 25 mmol m\(^{-2}\) d\(^{-1}\). This is higher than in the 29° to 23° S range of section BC2, despite showing a similar nutrient limitation index.
Figure 4.10: Brazil Current Section: a) biological saturation anomaly of oxygen; b) the weighted gas transfer coefficient; c) the net community production ($N$); d) nutrient limitation index, superimposed are the locations of the three Brazil current sections (BC1, BC2 and BC3).
4.4. Discussion

This discussion relates only to the data within the gyre section between 38° W and 8° E, as this is the focus of this study.

As described in the results we observed a consistent supersaturation of O₂ with respect to Ar (Figure 4.7c), which means that production exceeded respiration across the whole gyre. When accounting for the entrainment of O₂ from below the mixed layer the net community production of O₂ was, on average ± standard deviation, 10±3 mmol m⁻² d⁻¹ (Figure 4.7e).

4.4.1. Net community production

To understand what was driving net production in the gyre, I compared the nutrient limitation index and other variables to N (Figure 4.11). I found no relationship between sea surface temperature, salinity or chlorophyll a and N. In all three cases, the correlation coefficient of determination (r²) for a linear relationship was smaller than 0.01. Overall, salinity across the gyre showed no relationship to N, but when I considered only data with lower salinities (between 35.5 to 36.6), which corresponded to data east of 10° W until the edge of the Benguela section, the relationship was strong (r² = 0.74). This lower salinity signal is a tracer of the Benguela upwelling (see low salinities in the Benguela section in Figure 4.5b) and so it is the availability of nutrients as seen in the lower values of zlim (indicating available nutrients), and thus the high values of N in the surface water. Although I expected to find a positive relationship between the surface concentrations of chlorophyll a and N, no clear relationship existed, based on the data available.

The correlation between nutrient limitation index, zlim, and N was weak (r² = 0.15). However, I observed different trends within each of three discrete sections of nutrient limitation index: the first for -50 < zlim/m ≤ 0 (not nutrient limited), the second for 0 < zlim/m ≤ 50 (nutrient limited) and the third for zlim/m > 50 (highly nutrient limited). When the relationship with N was re-analysed within each section category, no clear relationship was found for 0 < zlim/m ≤ 50, but r² were of 0.29 and 0.30 were found for -50 < zlim/m ≤ 0 and zlim/m > 50, respectively. Such negative relationships were expected for the whole of the gyre.

A possible reason for the weak relationships between N with c(chl a) and zlim could be due to the difference in integration times of c(chl a) and zlim. While they are measurements of the conditions at the specific time of sampling, N integrates over the oxygen gas exchange between mixed layer and atmosphere, which was approximately 15 days.
To investigate the relationship between $N$ and wind speed, it would not have been appropriate to compare $N$ with $k_w$ because $F_{bio}$ (as a component of $N$) directly depends on $k_w$. Therefore, I compared $\Delta(O_2/Ar)$ with $k_w$. A negative relationship was found with greater values of $\Delta(O_2/Ar)$ corresponding to lower values of $k_w$, with $r^2 = 0.34$. The opposite relation was expected because stronger winds were thought to increase turbulence and introduce nutrients into the mixed layer. It appears instead that the increased wind tends to lead to more outgassing, which reduces $\Delta(O_2/Ar)$ for constant $N$.

A useful comparison here is also the $f$ ratio. The $f$ ratio was first proposed by Eppley and Peterson (1979) and was calculated as the ratio of new production measured by incubation of a sample with $^{15}$N-labelled nitrate over net primary production as measured by $^{14}$C incubations. This term would give information of the amount of organic matter available for export. Hendricks et al. (2004) proposed the use of $f$ ratios expressed by the $N/G$ as measured by $\Delta(O_2/Ar)$ and $O_2$ isotopologues.

No relationship was found between $f$ and $N$ ($r^2 < 0.01$), despite the fact that $f$ is calculated from the ratio $N/G$, highlighting that $N = 10 \pm 3$ mmol m$^{-2}$ d$^{-1}$ was not very variable whereas the variation in $G = 173 \pm 97$ mmol m$^{-2}$ d$^{-1}$ was 56%.

Figure 4.11: Comparison smoothed (moving average of 3.3 h) net community production ($N$) and smoothed biological oxygen saturation anomaly, $\Delta(O_2/Ar)$ with other parameters: a) $N$ versus sea surface temperature ($\theta_o$); b) $N$ versus sea surface salinity $S_o$; c) $N$ versus surface concentration of chlorophyll $a$; d) $N$ versus nutrient limitation index ($z_{lim}$); e) $\Delta(O_2/Ar)$ versus gas transfer ($k_w$); f) $f = \Delta(O_2/Ar)/g$ versus $N$. 88
(2) Regarding the origin of the nutrients feeding net phytoplankton production, it seems that the gyre section can be considered to consist of two different sections according to N$_2$ fixation rates and $\delta^{15}$N, PON (Figure 4.9): one west of 10° W and one east of 10° W. The section to the west had high N$_2$ fixation rates, ranging from >0.5 to 0.1 nmol l$^{-1}$ d$^{-1}$, and $\delta^{15}$N, PON) < -2 ‰, both of which indicate that N$_2$ fixation is an important process in the western portion of the gyre. The section east of 10° W had low N$_2$ fixation rates, <0.1 nmol l$^{-1}$ d$^{-1}$, and higher $\delta^{15}$N, PON) >2 ‰. This longitudinal separation seems to match that of the $z_{lim}$ (Figure 4.6-b). West of 10° W, $z_{lim}$ was generally greater than 50 m (thus making this region NO$_3^-$ limited or high nutrient stressed), whereas moving east of 10° W, $z_{lim}$ starts to decrease. While areas in the western portion were nutrient limited (specifically NO$_3^-$ limited), the edge with the Benguela section had areas with no nutrient limitation. Therefore, it seems that production east of 10° W is based more on NO$_3^-$ and to the west based more on N$_2$ fixation. Atmospheric nutrient deposition may play a role in both parts.

4.4.2. Previous measurements on N and G in the SATL

(3) Previous studies of the metabolic balance of the South Atlantic Tropical Gyre (SATL) have been carried out by using light and dark O$_2$ incubation techniques (Gist et al., 2009; González et al., 2002; Serret et al., 2001). All three studies measured instantaneous rates of net community production; therefore this methodology was restricted to just the production and respiration during the incubation period in the bottle (7 or 24 h). Measuring the rates of O$_2$/Ar presents an advantage over this earlier technique for several reasons: it has no bottle effects; O$_2$/Ar evaluates the N over periods of weeks, the time that takes to ventilate the mixed layer, which in this case was of about 15 days; and, finally, the rate of measurements is higher than in any of the previous studies, as it measures continuously in the mixed layer.

Among previous studies (Table 4.1), the lowest levels of N were recorded by González et al. (2002). These values, which differed substantially from those of the other studies, were recorded from measurements taken at locations at the western edge of the gyre, so it is possible that these data may not have been collected strictly within the gyre. Serret et al. (2006) defined the gyre as net autotrophic in the two springs that he was there. Gist et al. (2009) recorded a similar pattern but with values of N that were very close to a net balance, with 5 mmol m$^{-2}$ d$^{-1}$. In autumn, Gist et al. (Gist et al., 2009) found the gyre to be net heterotrophic, with a rate of -14 mmol m$^{-2}$ d$^{-1}$. 

Measurements of $O_2$/Ar showed a supersaturation, indicating that at least at the time of sampling all of the gyre was net autotrophic. Because the $O_2$/Ar method averages $N$ over time of the exchange of $O_2$ with the atmosphere this means that the gyre was net autotrophic for the period between sampling and 15 days before (the time it takes to exchange the mixed layer calculated as the ratio of $z_{mix}/k_w$).

### Table 4.1: Results of net community production ($N$) from previous studies and this one in the South Atlantic gyre.

<table>
<thead>
<tr>
<th>Reference</th>
<th>no. of stations</th>
<th>season</th>
<th>$N$ (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Technique used</th>
<th>lat (° N)</th>
<th>lon (°E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>González et al. 2002*</td>
<td>2</td>
<td>S</td>
<td>-44.5 ± 130</td>
<td>$O_2$ in vitro 7 h</td>
<td>5 to 32</td>
<td>-26 to -44</td>
</tr>
<tr>
<td>González et al. 2002*</td>
<td>2</td>
<td>A</td>
<td>-117 ± 135</td>
<td>$O_2$ in vitro 7 h</td>
<td>5 to 32</td>
<td>-26 to -44</td>
</tr>
<tr>
<td>Serret et al. 2006</td>
<td>5</td>
<td>S</td>
<td>20 ± 3</td>
<td>$O_2$ in vitro 24 h</td>
<td>10 to 34</td>
<td>-16 to -54</td>
</tr>
<tr>
<td>Gist et al. 2009</td>
<td>28</td>
<td>S</td>
<td>5 ± 26</td>
<td>$O_2$ in vitro 24 h</td>
<td>10 to 35</td>
<td>-3 to -35</td>
</tr>
<tr>
<td>Gist et al. 2009</td>
<td>28</td>
<td>A</td>
<td>-14 ± 26</td>
<td>$O_2$ in vitro 24 h</td>
<td>10 to 35</td>
<td>-3 to -35</td>
</tr>
<tr>
<td>This study</td>
<td>continuous</td>
<td>A</td>
<td>13 ± 3</td>
<td>$O_2$/Ar in situ</td>
<td>24</td>
<td>-50 to 11</td>
</tr>
</tbody>
</table>

(*) as reported by Serret et al. 2006

Bottle incubation techniques aim to measure net community production ($N$) by enclosing a water sample in bottles and recording the change of $O_2$ concentration under dark and light conditions. $N$ is defined as the difference in concentration between the light condition and the dark condition. This technique assumes that the trophic composition of the water sample is and will remain the same as that of the sample from which it was taken.

Gieskes et al. (1979) and Harris (1986) found high rates of photochemical pigment destruction in enclosed samples, and this destruction was higher in smaller water samples (30 ml) than in larger samples (4 l), in which the reduction in photochemical pigment was nearly negligible. Fernández et al. (2003) found that the concentrations of important phytoplankton species in oligotrophic Atlantic waters – *Prochlorococcus* spp. and picoeukaryotes (Marañón et al., 2000) – declined dramatically (>50 %) after only two hours of incubation. Moreover, Calvo-Díaz et al. (2011), examining the abundance of the representative community for oligotrophic waters, observed not only a decreased in *Prochlorococcus* and picoeukaryotes over the time of incubation but also, in some experiments, an increase in the total concentration of heterotrophic bacteria.
On the other hand, measurements in other gyres using the same technique of measuring \(O_2/\text{Ar}\) ratios that was used in this study have found similar results to the ones presented here. For instance, Quay et al. (2010) at station ALOHA near Hawaii found an average \(N\) of 14±4 mmol m\(^{-2}\) d\(^{-1}\) during a time series spanning from March 2006 to February 2008. Luz and Barkan (2009) found at BATS near Bermuda values of \(N\) ranging from 6 to 8.3 mmol m\(^{-2}\) d\(^{-1}\) over a time series between May-October 2000. Juranek et al. (2012) collected data during 4 different cruises in the North Pacific Gyre in the spring 2003 and 2006 and summer 2003 and 2008 and recorded an average \(N\) of 8.3±1.3 mmol m\(^{-2}\) d\(^{-1}\). All these results for \(N\) ranging from 6 to 14 mmol m\(^{-2}\) d\(^{-1}\) compared well with these estimates of 10±3 mmol m\(^{-2}\) d\(^{-1}\).

Therefore, it is likely that measurements of \(N\) made by bottle incubation techniques might be overestimating the respiration of these communities, at least in oligotrophic regions, due to a decrease of the autotrophic components of the community. Hence, it is preferable to derive \(N\) from \textit{in situ} measurements such as \(O_2/\text{Ar}\) data.

### 4.4.3. Gross oxygen production

(4) Using the isotopic composition of dissolved \(O_2\), I estimated gross oxygen production \((G)\), calculated using the dual delta method proposed by Kaiser (2011b) and using \(\delta_{\text{VSMOW}}\) as reported by Kaiser and Abe (2012). Following from this an average \(g = 0.28±0.13\) and \(G = 173±97\) mmol m\(^{-2}\) d\(^{-1}\) was obtained for the gyre.

As explained in Chapter 1, \(g\) can be calculated using the dual delta method or the older approximate method by Luz and Barkan (Luz and Barkan, 2000) based on the \(^{17}\text{O}\) excess, \(\Delta(^{17}\text{O})\). Here I present results using both approaches:

\[
g_{LB} = \frac{^{17}\Delta_{\text{dis}} - ^{17}\Delta_{\text{sat}}}{^{17}\Delta_{\text{p}} - ^{17}\Delta_{\text{dis}}} \tag{4.11}
\]

\[
g_k = \frac{(1 + \Delta(O_2))(^{17}e_E - y_R^{18}e_E) - \frac{^{17}e_l - ^{17}\delta}{1 + ^{17}\delta} + y_R \frac{^{18}e_l - ^{18}\delta}{1 + ^{18}\delta}}{\frac{^{17}\delta_{\text{p}} - ^{17}\delta}{1 + ^{17}\delta} - y_R \frac{^{18}\delta_{\text{p}} - ^{18}\delta}{1 + ^{18}\delta}} \tag{4.12}
\]
Chapter 4. Oxygen production in the subtropical South Atlantic

The value of \( g \) not only varies according to the formula used to calculate it, but is also strongly influenced by the choice of parameters needed to calculate it (Kaiser, 2011b; Prokopenko et al., 2011). Among these parameters are \( ^{17}\delta p \) and \( ^{18}\delta p \), which hereafter are referred to as \( *\delta p \) – where “*” stands for 17 or 18. This \( *\delta p \) is calculated from the isotopic composition of the source water \( (*\delta_{\text{VSMOW}}) \) and the photosynthesis fractionation \( (*\varepsilon_p) \). As explained in Chapter 1, there is disagreement on the values of \( *\delta_{\text{VSMOW}} \), with values reported by Kaiser and Abe (2012), K&A) of \( ^{17}\delta_{\text{VSMOW}} = -12.102 \, \text{‰} \) and \( ^{18}\delta_{\text{VSMOW}} = -23.647 \, \text{‰} \), and the values reported by Luz and Barkan (2011), L&B) of \( ^{17}\delta_{\text{VSMOW}} = -11.883 \, \text{‰} \) and \( ^{18}\delta_{\text{VSMOW}} = -23.324 \, \text{‰} \). Values reported by Barkan and Luz (2005) are similar to those of Kaiser and Abe (2012), once corrected for mass-dependent fractionation effects. Therefore, I examine how \( G \) is impacted by using the approximate equation and the choice of \( *\delta_{\text{VSMOW}} \) reported by two previous studies, K&A (2012) and B&L (2011).

Figure 4.12 shows that the bias due to the approximate calculation method would have been small for the present dataset. Greater differences were encountered when comparing the results using the \( *\delta_{\text{VSMOW}} \) reported by K&A and the one from B&L (2011). On average, \( G \) based on \( *\delta_{\text{VSMOW}} \) K&A value was 30% higher than if based on L&B. This relative difference ranged from 26 % to 37 %.

In view of this comparison, the choice of \( *\delta_{\text{VSMOW}} \) appears much more relevant than the choice of formulae and would therefore generate greater uncertainty than the selection of the formula to calculate \( g \), the influence of which can be considered negligible for this dataset.

![Figure 4.12: Comparison of \( G \) using different approaches indicated in the legend. These differences are due to: using the exact formula (dual delta method) proposed by Kaiser (2011b) (closed diamonds) or the approximated formula proposed by Luz and Barkan (2000) (open circles) and the choice of \( *\delta_{\text{VSMOW}} \) of by Barkan and Luz (2011) or by Kaiser and Abe (2012), in red and black, respectively.](image-url)
(5) As for $N$ and $\Delta (O_2/Ar)$ in Figure 4.11, we compared $G$ and $g$ to different potential predictor variables (Figure 4.13). We observed no relationship ($r^2$ never > 0.06) between $G$ or $g$ and $S_0$, $S_0$ or surface chlorophyll $a$ concentrations. The lack of a relationship between $c (chl-a)$ and $G$ could be due to the different integration times of the measurement: $G$ integrates over the residence time of $O_2$ over the mixed layer (15 days for the gyre) and $c (chl-a)$ more closely reflects the shorter lifetime of the phytoplankton community.

Overall, the relationship between $z_{lim}$ and $G$ was very weak ($r^2 = 0.05$). When the $z_{lim}$ was subdivided into three different depth sections, $r^2$ increased to 0.11 for data from above 50 m, while no better relationship was found for the $z_{lim}$ between 0 and 50 m. Only two data points were available for areas with no nutrient limitation ($z_{lim}<0$), so no regression was done. In any case, the lowest values of $G$ were associated with mixed layer under low to high nutrient limitation, whereas the high values of $G$ were associated with low to no nutrient limitation. Also, no relationship was found between $g$ and $k_w$ ($r^2=0.01$).

What was striking was an unexpected strong inverse relationship between $G$ and $f$ ($r^2=0.83$) (Figure 4.13f). The expected outcome was that for high values of $G$, $f$ would also be high. Instead, the highest $f$, up to 0.8, was found in samples with the lowest $G$, and in samples with high $G$ (above 300 mmol m$^{-2}$d$^{-1}$), $f$ was < 0.05. This relationship was not linear, but hyperbolic, and it explains 83% of the variability in $G$ present in the data. Due to the low variability of the $\Delta (O_2/Ar)$ compared to $g$, $f$ can be approximated by $6 \text{ mmol m}^{-2} \text{ d}^{-1} / G$. 

Figure 4.13: Comparison of different predictor variables to gross oxygen production ($G$) and $g$. a) $G$ versus sea surface temperature ($\theta_o$); b) $G$ versus sea surface salinity; c) $G$ versus surface concentration of chlorophyll $a$ – (chlo-a); d) $G$ versus nutrient limitation ($z_{lim}$ lines in the figure added to help visualize three different relationships between $G$ and $z_{lim}$); e) $g$ versus gas transfer ($k_w$); and f) $G$ versus the $f$ ratio ($f=\Delta(O_2/Ar)/g$).

(6) Regarding the analysis of FRRF data presented as photosystem quantum efficiency ($Fv/Fm$, Figure 4.8-b), it appears that the area to the west of the Greenwich meridian has a more stable $Fv/Fm$ and the area to the east is more variable. I hypothesize that this difference across different regions of the gyre is due to a different phytoplankton species composition. Traditionally, $Fv/Fm$ was interpreted as an indicator of nutrient or light stress (Huang et al., 2012) (Cassar et al., 2009). On the other hand, Sigg et al. (2009), proposed that $Fv/Fm$ was not only an indicator of nutrient stress but also was dependant on the taxonomic composition of the sampled area. If this is correct, the ecosystems in the two sections of the gyre should be differentiated by their respective nutrient availabilities – poorer in nutrients to the west and higher concentrations of nutrients to the east, which is influenced by the Benguela current (Figure 4.8-b). That is why my findings – cells to the west seemed less stressed, with $Fv/Fm$ values of 0.45 to 0.6, while the lower values of 0.3 to 0.5 recorded in the east – were unexpected. This might be explained by higher activity of Photosystem II (PSII) to the west, where cells are adapted to low nutrient concentrations and manage the excess of light by mechanisms like the Mehler reaction in order to alleviate damaging effects of high rates of
photon absorption by PSII (Grossman et al., 2010). One explanation of this unexpected result could be that to the east the autotrophic organisms are typical of high-nutrient ecosystems and when entering the gyre they experience high stress leading to low values of \( F_v/F_m \). On the other hand, Sugget et al. (2009) found in laboratory experiments that when cells growing in nutrient-poor conditions were fertilized with N, their \( F_v/F_m \) decreased; therefore, it is possible that cells from the gyre, when exposed to higher concentrations of nitrogen from the upwelling, might experience a decrease in \( F_v/F_m \).

4.4.4. Previous measurements of gross production

(7) The \( G \) measurements recorded by different authors (Table 4.2), were also measured in different seasons and different years, which is important to remember when comparing them. Marañón et al. (2003) found an average for two spring and two summer seasons of 38 mmol m\(^{-2}\) d\(^{-1}\) O\(_2\), which is a lower value than the average of the two seasons as measured by Gist et al. (2009) of 57 mmol m\(^{-2}\) d\(^{-1}\) O\(_2\). Data for a single season recorded by Serret et al. (2009) and Gist et al. (2009) seem to be much more similar to each other than either is to those of Marañón. Considering that all those studies integrated production within the euphotic layer, their values of \( G \) are very small compared to the results of the present study, which do not integrate the entire euphotic layer and were restricted to the mixed layer. The fact that the method used here considered only production within the mixed layer implies that I could, if anything, have underestimated production. However, my values of 177 mmol m\(^{-2}\) d\(^{-1}\) were nearly four times greater than those measured by Gist et al. (2009). My findings for \( G \) have a greater uncertainty than those for \( N \) so a comparison with previous data has to be much more cautious.

Several factors increase the uncertainty for valuing \( G \): (1) it is possible that the differences observed could be attributed to inter-annual variability. (2) The entrainment from below the mixed layer might enhance the difference in \( G \) values, and, as discussed earlier, this is probably at about 4% assuming a constant mixed layer; if this is the case then it is unlikely to have caused the difference with the measurements of previous studies. But if the mixed layer has deepened then \( O_2 \) from below the mixed layer has entrained, this process was modelled by Nicholson et al. (2012) and was accounted to be of 60% and 80% of the observed values at BATS and HOT respectively.

(3) As with the variability in \( g \) values, depending on the parameters used to calculate it, I showed that a difference of up to 30% between \( G \) calculated with the *\( \delta_{VSMOW} \) reported by
L&B (122 mmol O\(_2\) m\(^{-2}\) d\(^{-1}\)) and that calculated by K&A (177 mmol O\(_2\) m\(^{-2}\) d\(^{-1}\)). (4) The wind speed parameterisation accounts for 30 % of the error in G.

Finally, (5) it is plausible that the Mehler reaction might be an important mechanism regulating to the light stressed cells in this area (Grossman et al., 2010). This reaction might show an increase in the G of up to 10-60% when actually there is no real fixation of C or release of O\(_2\) (Kana, 1990; Kana, 1992). This reaction happens in the PSII, which would increase the likelihood that it would produce the high values of the \(F_v/F_m\) seen (Figure 4.8-b).

### Table 4.2: Results reported for G (gross oxygen production) from previous studies and data from this study in the South Atlantic Gyre. Columns represent: the reference source of the data; the number of stations for which the study reported values; the season with “S” and “A” standing for spring and autumn; the value of G as the gross oxygen production; the technique used; and latitude and longitude of the locations of the measurements.

<table>
<thead>
<tr>
<th>Reference</th>
<th>no. of st</th>
<th>season</th>
<th>(G) (mmol m(^{-2}) d(^{-1}))</th>
<th>Technique used</th>
<th>lat (° N)</th>
<th>lon (°E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marañón et al. 2003</td>
<td>25</td>
<td>S &amp; A</td>
<td>38 ± 18</td>
<td>Integrated production rate ((^{14})C 7 h), (^*)PQ=2.7</td>
<td>-8 to -32</td>
<td>-28 to -44</td>
</tr>
<tr>
<td>Serret et al. 2006</td>
<td>5</td>
<td>S</td>
<td>60 ± 8</td>
<td>(O_2) in vitro incubation for 24 h (GP)</td>
<td>-10 to -34</td>
<td>-16 to -54</td>
</tr>
<tr>
<td>Gist et al. 2009</td>
<td>28</td>
<td>S</td>
<td>72 ± 26</td>
<td>(O_2) in vitro incubation for 24 h (GP)</td>
<td>-10 to -35</td>
<td>-3 to -35</td>
</tr>
<tr>
<td>Gist et al. 2009</td>
<td>28</td>
<td>A</td>
<td>42 ± 26</td>
<td>(O_2) in vitro incubation for 24 h (GP)</td>
<td>-10 to -35</td>
<td>-3 to -35</td>
</tr>
<tr>
<td>This study</td>
<td>50</td>
<td>A</td>
<td>177 ± 98</td>
<td>isotopic composition of dissolved (O_2)</td>
<td>-24.00</td>
<td>-40 to 10</td>
</tr>
</tbody>
</table>

\(^*\) Photosynthetic Quotient (PQ) used here is taken from Marra (2002).

When the effect that the Mehler reaction might have on G is considered, it is very likely that it is this reaction that is responsible for the abnormal relationship between \(f\) and G depicted in Figure 4.13-d. This relationship would initially suggest that greater \(f\) ratios occur at very low values of \(G\), which is counterintuitive. This relationship relies mainly on the variability in \(G\). It is very likely that the more light stressed the cell might be, the smaller the \(\Delta(O_2/Ar)\) (thus \(N\)), and, in opposing behaviour, the greater the value of \(G\), though probably due to Mehler reaction as a mechanism for coping with excess of light as opposed to C fixation. The relevance of the Mehler reaction in oligotrophic areas is assumed to be higher than in other areas where there are higher nutrient concentrations and less light, but the magnitude of variability in the influence of this reaction is unknown, with reported values of Mehler reaction ranging from 10% to 60% of all the apparent C fixation (Kana, 1990; Kana, 1992).
There are studies in other oligotrophic regions using O$_2$ isotopologues. Juranek et al. (2012) recorded $G$ values of 89±9 mmol m$^{-2}$ d$^{-1}$ for the North Pacific subtropical gyre during six different cruises. Juranek et al. (2010) recorded $G$ values of 98±8 and 115±7 mmol m$^{-2}$ d$^{-1}$ for the North and South Pacific gyre, respectively, during 2 cruises. Quay et al. (2010) from a time series at the ALOHA site obtained an average of 81±39 mmol m$^{-2}$ d$^{-1}$ during the Northern summer. These measurements are far from my estimate of 177±98 mmol m$^{-2}$ d$^{-1}$, but if I calculate $G$ using L&B values for *δ$_{VSMOW}$ (as previous studies have used, albeit implicitly) I obtain 122±63 mmol m$^{-2}$ d$^{-1}$, a value within the standard deviation of the other studies.

4.5. Conclusions

(1) A gradient from west to east was observed in $\theta_0$, $S_0$ and associated with it there was a gradient in c(O$_2$) and $\Delta$(O$_2$/Ar). The sea-to-air flux of O$_2$ was 16±4 mmol m$^{-2}$ d$^{-1}$.

(2) The biological O$_2$ saturation anomaly derived from continuous measurements showed a consistent supersaturation across the gyre. When accounting for entrainment into the mixed layer, this gave an average $N$ of 10±3 mmol m$^{-2}$ d$^{-1}$.

(3) No clear relationship was found between $\theta_0$, $S_0$, c(chl a) or $f$ ratio and $N$. A weak correlation ($r^2 = 0.30$) was found between $N$ and $z_{lim}$ for highly stressed cells with $z_{lim} > 50$ m, with higher values of $N$ associated with less severe nutrient stress. Also a higher $r^2 = 0.34$ was found when comparing $\Delta$(O$_2$/Ar) to $k_w$ but unexpectedly the relationship was negative.

(4) Based on the $\delta^{15}$N of particulate organic nitrogen and N$_2$ fixation rates the gyre seemed to be separated in 2 distinct areas one west of 10 °W where N$_2$ fixation was higher and low values of $\delta^{15}$N. To the east, N$_2$ fixation rates were negligible and $\delta^{15}$N indicates that the source of nitrogen is likely to be NO$_3^-$, with a gradient from 10° W to the Benguela section, probably influenced by upwelling.

(5) Other metabolic studies of the south Atlantic gyre were all done by light and dark bottle incubations and all $N$ estimates were lower than mine. This difference is attributed to bottle effects for which studies have reported a change in the community when enclosed in bottles. Our measurements matched well with other measurements in other similar regions using the O$_2$/Ar measurements.

(6) Gross oxygen production was estimated to be 177±98 mmol m$^{-2}$ d$^{-1}$ ($n = 50$) when using the dual delta method proposed by Kaiser (2011b) and using *δ$_{VSMOW}$ as reported by
Kaiser and Abe (2012). $G$ calculated with $\delta_{\text{VSMOW}}$ as reported by Luz and Barkan (2011) is 30% lower. The formula used for the calculation of $g$ did not have a great impact on $G$.

(7) Compared with other published data in the south Atlantic gyre our estimates of $G$ were higher. The difference could be attributed to several causes. One of these uncertainties lies in $k_w$ which has an impact on $G$ of ±30%. Another possibility is entrainment, which can be by eddy diffusion or by mixed layer deepening. For eddy diffusion, this was estimated to be 4% for one station for which isotope samples were collected at 6° E. If deepening of the mixed layer has occurred then past signals in photosynthesis in the $O_2$ would enhance the $G$ measured in the mixed layer. Whether these mechanisms are relevant we cannot know, but Nicholson modelled it to be between 60 to 80% for BATS and HOT respectively. Finally but not least important it is likely that Mehler reaction might be playing a role in increasing the isotopic measurements made from the isotopes and $F_o/F_m$ (Grossman et al., 2010; Kana, 1990; Kana, 1992) but not the real C fixation, the range of this reaction is unknown and has been reported to be between 10% to 60%.

(8) Despite these uncertainties our measurements compared well with those in the literature for other gyres using the isotopic composition of the $O_2$ dissolved in the mixed layer if using $\delta_{\text{VSMOW}}$ of Luz and Barkan (2011) as the other studies have similar results.
Chapter 5. Measurements of production in a North Atlantic Bloom
5.1. Introduction

Despite its relatively small area, covering 15% of the global ocean, the North Atlantic region absorbs 23% of the total anthropogenic carbon (C) uptake by the oceans (Sabine et al., 2004). This is due to the cooling of the surface waters during northward transport, which increases CO$_2$ solubility, and the drawdown of CO$_2$ by biological activity (Takahashi et al., 2009).

This biological activity is most intense during the spring bloom. The mechanisms that trigger this bloom are still under debate. The first theory was put forward by Sverdrup (1953), who hypothesised that the initiation of the bloom would occur when spring warming would decrease the depth of the mixed layer to less than the critical depth. Since then, several studies have challenged this hypothesis, suggesting different mechanisms for the triggering of the spring bloom. Waniek (2003) postulated that episodic events of stratification intercalated with storms allowing the input of nutrients to sustain the blooms. On the other hand, Behrenfeld (2010) put forward that the initiation of the bloom would start when growth and grazing of phytoplankton are decoupled, so that the bloom would start in winter time when the mixed layer is deeper than the euphotic zone and predators and prey have less chances to meet. In 2011, Taylor and Ferrari (2011) suggested that a weakening of turbulent mixing would enable the accumulation of phytoplankton growth. More recently, Mahadevan et al. (2012) presented a different hypothesis tested with the data of the bloom in spring 2008. It states that the horizontal gradient of density between the colder north and warmer south would generate mixed layer eddies where stratification would occur and where phytoplankton blooms would develop.

The evolution of the bloom was described by Sieracki et al. (1993) for the North Atlantic Bloom Experiment (NABE) in 1989. Initially, the bloom is formed mainly by diatoms, which prosper until they consume most of the silicate. It is then that there is a shift in the community which changes to small phytoflagellates. Towards the end of the diatom bloom, Sieracki et al. (1993) found a large amount of detritus in the water column (“calculated as the difference between the total particulate elemental carbon measured on glass-fiber filters and the sum of the carbon in all the biomass components”), which was absent in the second stage with the phytoflagellates and they attributed this increase in the detritus to material produced by the diatoms that did not sink with them.
Primary productivity has been measured during several studies. One of the first was in the NABE experiment as part of Joint Global Ocean Flux Study (JGOFS). In spring 1989 and 1990 net primary production was found to be between 48 to 105 mmol m$^{-2}$ d$^{-1}$ C (with a standard deviation of the four different studies of 18 mmol m$^{-2}$ d$^{-1}$ C) by means of $^{14}$C uptake in bottle incubations (Bender et al., 1992; Bury et al., 2001; Joint et al., 1993; Martin et al., 1993).

Previous estimates of net community production ($N$) have been derived by several methods, including; $^{234}$Th budgets, daily changes in $O_2$ and $CO_2$, $NO_3^-$ drawdown, DIC drawdown, $PO_4^{3-}$ drawdown, $O_2$ budget and POC budget (Bender et al., 1999; Buesseler et al., 1992; Chipman et al., 1993; Robertson et al., 1993; Sambrotto et al., 1993). Such studies for NABE in May 1989 experiment measured a range of $N$ from 5-90 mmol m$^{-2}$ d$^{-1}$ C with a mean of 47 mmol m$^{-2}$ d$^{-1}$ C.

In this chapter is described the biological flux of $O_2$ from the sea to the atmosphere during a spring bloom in the North Atlantic in 2008. Based on $O_2$ observations is shown the highly variable nature of the North Atlantic Bloom. As described in earlier studies, it is common to find different water masses with different biological conditions in close proximity.

This study was part of a project studying the bloom from a Lagrangian float which followed the same water mass, here is described the biological $O_2$ flux produced by this water mass, as measured on a ship, and compare it to the float measurements. Also, is discussed, based on flow cytometry (Mike Sieracki), biological $O_2$ production in two different stages of the bloom, the first one dominated by diatoms, followed by a second stage dominated by nanophytoplankton.

### 5.2. Methods

The data used for this study were collected on board of RV/Knorr in an area Southwest of Iceland centred at 61.4° N 26° W between 1 and 22 May 2008 (Figure 5.1). Data were collected for the analysis of $O_2$ and $O_2/Ar$ concentrations in surface waters for quantification of net community productivity ($N$). In addition, the isotopic composition of the $O_2$ dissolved in the water was measured for the determination of the gross production in terms of $O_2$ ($G$).

Continuous measurements from the underway sea water (USW) of $O_2$ and $O_2/Ar$ were collected, as well as discrete samples for the analysis of their $c(O_2)$ and evacuated bottles for $O_2/Ar$ and isotopic composition of the $O_2$ dissolved in the water. From the Niskins on the CTD,
discrete samples for the measurement of O$_2$ concentration were collected to calibrate the O$_2$ sensor on the CTD. Discrete evacuated bottle samples were also taken for Paul Quay and for me from both the CTD and the USW for analysis of their O$_2$ isotopic composition and O$_2$/Ar concentrations.

Ancillary continuous measurements taken in the underway sea water supply (USW) were the sea surface temperature ($\theta_0$), salinity ($S_0$) and the concentration of chlorophyll a (c(chl a)). Sea surface temperature from the USW was calibrated against the temperature measured by the CTD sensor in surface waters. This procedure was repeated for the salinity. Chlorophyll a concentrations were measured continuously by Giorgio Dall’Olmo and Toby Westberry by hyperspectral absorption-attenuation meter (ACs) (Westberry et al., 2010). The phytoplankton species composition was studied at selected CTD stations (Mike Sieracki with a Becton Dickinson FACScan flow cytometer (Sieracki and Poulton, 2011)).

O$_2$ optode USW concentrations - c(O$_2$) - were calibrated against discrete Winkler samples taken from the USW (Figure 5.2). The O$_2$ calibration is explained in detail in Chapter 3. In brief, the raw signal from the optode (DPhase) was compared to the discrete Winkler measurements. To do so, the c(O$_2$) obtained by the discrete sampling were converted to

Figure 5.1: Map showing the location of the study. Blue colours represent depths in m as indicated by the colourbar. The black colouring represents depths above sea level, in this case Iceland. The red line represents the cruise track.
DPhase using the inverted manufacturer-provided sensing foil calibration equation. From all the optode c(O₂) data, approximately 36% were disregarded, because of problems with bubbles or shut-down of the USW. The periods with bubbles display abnormal variability with very high values of O₂ concentration alternated with lower c(O₂) values, which were more in line with expectations. During the USW shut-down the O₂ concentration decreased over time on 4 May 2008 (year-day 125). The four periods with bubbles were 3-5 (year-day 124-126), 9-10 (year-day 130-131), 17-18 (year-day 138-139) and 19-22 (year-day 140-143) May, 2008. These periods were recognized when the c(O₂) of samples from the CTD was lower than that of the USW by more than 2.65 μmol kg⁻¹. These periods were not used for the study presented here.

The CTD O₂ sensor was calibrated by direct comparison with the discrete Winkler samples versus the sensor O₂ concentration reading. The O₂ data from the CTD was used for calculation of the change of c(O₂) in the pipes of the ship. On average there was net consumption of O₂ in the pipes of the R/V Knorr (Figure 5.3). This consumption was -0.6±1.0
μmol kg⁻¹ (mean±standard deviation) as measured by the discrete Winkler measurements from the Niskins and -0.91±1.12 μmol kg⁻¹ as measured by the sensor on the CTD. All data combined gave a net consumption of O₂ of -0.87±1.11 μmol kg⁻¹. This net consumption of O₂ in the pipes ($R_p$) accounted for 0.3% of the mean O₂ saturation concentration and was corrected for when calculating $\Delta(O_2)$, the oxygen saturation anomaly.

![Figure 5.3](image)

**Figure 5.3:** Change in calibrated O₂ concentration ($c(O_2)$) in the pipes measured as USW - CTD. Turquoise stars represent the calibrated $c(O_2)$ measured by the optode minus discrete $c(O_2)$ from samples collected from surface Niskin bottles. Green points correspond to the calibrated $c(O_2)$ measured by the optode minus surface measurements of the CTD sensor.

The oxygen saturation anomaly, $\Delta(O_2)$ was calculated using the continuous measurements of $c(O_2)$ in the USW with the equation below:

$$\Delta(O_2) = \frac{c(O_2)}{c_{sat}(O_2)} - 1 + R_p \quad (5.1)$$

Where $c(O_2)$ and $c_{sat}(O_2)$ are the concentration and saturation concentration at in situ conditions of O₂, respectively, and $R_p$ is the term that accounts for the 0.3% of respiration in the pipes.

The mixed layer depth ($z_{mix}$) was calculated as the depth at which the density was different by 0.01 kg m⁻³ from that at a reference depth of 10 m. The euphotic depth ($z_{eu}$) was calculated as the depth at which there is 1% of the surface irradiance.
The gas transfer coefficient was calculated as a weighted gas transfer coefficient ($k_w$) accounting for the wind speed history 60 days previously to the sampling, similarly as described by Reuer (2007) and explained in Chapter 3.

A gradient of $O_2$ occurred below the mixed layer, with generally lower $c(O_2)$ below the mixed layer, causing the $O_2$ in the mixed layer to diffuse downward to deeper waters (Figure 5.4-b). To calculate the “loss” of $O_2$ across the mixed layer, it was used a vertical eddy diffusivity ($k_v$) of $10^{-4}$ m$^2$ s$^{-1}$ (Moum and Osborn, 1986). The flux was calculated as:

$$ F_v = \frac{d(O_2)}{dz} k_v \quad (5.2) $$

Where $d(O_2)/dz$ is the change of $c(O_2)$ over depth between the bottom of the mixed layer and 10 m below the mixed layer and $k_v$ is the vertical eddy diffusivity.
Figure 5.4: Depth profiles of the density (a), c(O₂) (b) and Δ(O₂) (c) as measured by the CTD over time.
The solid black line is the mixed layer depth \( z_{\text{mix}} \) according to the 0.01 kg m\(^{-3}\) depth density difference criterion.
The gray line is the euphotic zone depth defined as the depth at which the irradiance is 1\% of that at sea surface.
The biological O₂ saturation anomaly, Δ(O₂/Ar), and the isotopic composition of dissolved O₂ (¹⁷δ and ¹⁸δ) were measured back on land in UEA’s Stable Isotope Laboratory for 53 discrete samples (37 from the USW and 16 from the CTD). In addition 32 samples for Paul Quay were collected which he measured independently at the University of Washington. For a comparison between these two laboratories for this study were collected 6 replicates at the same location and time. The samples were collected in 500 cm³ pre-evacuated flasks, poisoned with HgCl₂. The analytical procedures are described in detail in Chapter 3. The analysis determined Δ(O₂/Ar) and ¹⁷δ and ¹⁸δ of the samples, which were used to calculate N and G respectively. Below is described how to calculate Δ(O₂/Ar) and N. Afterwards is explained how g was calculated, from ¹⁷δ and ¹⁸δ values, as well as from G.

For the calculation of Δ(O₂/Ar):

\[ \Delta(O_2/Ar) = \frac{(O_2/Ar)}{(O_2/Ar)_{sat}} - 1 \] (5.3)

Where (O₂/Ar) and (O₂/Ar)_{sat} are the ratio of the O₂ and Ar concentrations, as measured at in situ conditions and at saturation.

A comparison of the Δ(O₂), as calculated from the continuous measurements of O₂ from the USW, and Δ(O₂/Ar) from the discrete samples, is presented in Figure 5.5. The slope of this relationship gives information on whether Δ(O₂) is mainly influenced by biological processes or not. In such relationship, a slope of 1 and an intercept of 0 with a high \( r^2 \) implies that all the supersaturation observed in the Δ(O₂) is due to biological processes. It was obtained a slope of 1.11±0.03 (slope±standard error) and an intercept of -0.23±0.24 % (intercept±standard error) with a high correlation (\( r^2=0.93 \), Figure 5.5), meaning that the Δ(O₂) deviates little from the Δ(O₂/Ar). Thus the biological processes affecting the c(O₂) are large compared to the physical processes. Therefore O₂ alone can be used as a proxy for biological activity.
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Figure 5.5: Comparison of the discrete $\Delta(O_2/Ar)$ ratios with the $\Delta(O_2)$ from the USW collected at the same time. Red dots represent the data from Paul Quay and black dots represent the data analyzed at UEA.

To estimate the physical contribution to the $c(O_2)$ observed, we calculated the Ar saturation anomaly, $\Delta(Ar)$, from the discrete measurements of $\Delta(O_2/Ar)$ and $\Delta(O_2)$ as:

$$\Delta(Ar) = \left(\frac{\Delta(O_2) - \Delta(O_2/Ar)}{1 + \Delta(O_2/Ar)}\right) \quad (5.4)$$

The mean $\Delta(Ar)$ was $0.44 \pm 0.67$ % (mean±standard deviation) and it ranged from -1.54% to 5.70%. This means that overall the physical processes contributed 0.44% to the total $\Delta(O_2)$, which was subtracted from the $\Delta(O_2)$ using the analogous equation:

$$\Delta(O_2/Ar) = \left(\frac{\Delta(O_2) - \Delta(Ar)}{1 + \Delta(Ar)}\right) \quad (5.5)$$

The results from the direct comparison of $\Delta(O_2/Ar)$ and $\Delta(O_2)$ (Figure 5.5) show that $\Delta(O_2)$ can be used for calculating the biological O$_2$ air-sea flux, if a correction is made for the 0.44% of the O$_2$ anomaly that is due to physical processes (as obtained from $\Delta(Ar)$).

The biological air-sea flux of O$_2$ was calculated as:
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\[
F_{\text{bio}}(O_2/Ar) = \Delta(O_2/Ar) \ k_w \ c_{\text{sat}}(O_2) 
\]  
(5.6)

Where \( k_w \) is the weighted gas transfer coefficient, calculated using a weighted historical wind speed value for the previous 60 days of sampling (as explained in Chapter 3).

Assuming only vertical diffusion of \( O_2 \) from the mixed layer to the waters below \((F_v)\) and no horizontal exchange, \( N \), would be calculated as:

\[
N(O_2/Ar) = F_{\text{bio}}(O_2/Ar) - F_v 
\]  
(5.7)

The ratio \( g \) between gross \( O_2 \) production and gross \( O_2 \) influx from the atmosphere can be calculated with \( g \) (which is the ratio of gross oxygen production \( G \) over \( k_w c_{\text{sat}}(O_2) \)) with the equation described by Kaiser (2011b):

\[
g = \frac{(1 + \Delta(O_2))(^{17}\varepsilon_E - \gamma_R^{18}\varepsilon_E) - \frac{^{17}\varepsilon_I - ^{17}\delta}{1 + ^{17}\delta} + \gamma_R \frac{^{18}\varepsilon_I - ^{18}\delta}{1 + ^{18}\delta}}{\frac{^{17}\delta_p - ^{17}\delta}{1 + ^{17}\delta} - \gamma_R \frac{^{18}\delta_p - ^{18}\delta}{1 + ^{18}\delta}}
\]  
(5.8)

Where \( \Delta(O_2) \) is the saturation anomaly of \( O_2; ^{17}\varepsilon_E \) and \( ^{18}\varepsilon_E \) are the kinetic \( ^{17}O/^{16}O \) and \( ^{18}O/^{16}O \) fractionation during \( O_2 \) evasion from sea to air; \( \gamma_R \) is the \( ^{17}\varepsilon_E/^{18}\varepsilon_E \) ratio of respiratory \( ^{17}O/^{16}O \) and \( ^{18}O/^{16}O \) fractionation; \( ^{17}\varepsilon_I \) and \( ^{18}\varepsilon_I \) are the kinetic \( ^{17}O/^{16}O \) and \( ^{18}O/^{16}O \) fractionation during \( O_2 \) invasion from sea to air; \( ^{17}\delta \) and \( ^{18}\delta \) relative \( ^{17}O/^{16}O \) and \( ^{18}O/^{16}O \) differences between measured \( O_2 \) and air \( O_2 \); and \( ^{17}\delta_p \) and \( ^{18}\delta_p \) relative \( ^{17}O/^{16}O \) and \( ^{18}O/^{16}O \) differences between photosynthetic \( O_2 \) and air \( O_2 \).

Gross oxygen production, \( G \), was then calculated using:

\[
G = g \ k_w c_{\text{sat}}(O_2) 
\]  
(5.9)
Where $g$ is defined in equation 5.8; $k_w$ is the weighted gas transfer coefficient and $c_{\text{sat}}(O_2)$ the saturation concentration of $O_2$ at \textit{in situ} conditions.

5.3. Results

The mean $c(O_2)$ for the surface waters throughout the whole cruise was of 296.9±6.8 μmol kg$^{-1}$ with a minimum of 278.0 μmol kg$^{-1}$ and a maximum of 319.7 μmol kg$^{-1}$ (Figure 5.6-a). Sharp changes in $c(O_2)$ like on year-day 129 from 295 to 310 μmol kg$^{-1}$ over a distance of 0.7 nm show the high variability in the area. Sea surface temperature ($\theta_0$) ranged between 8.0°C to 9.8°C with sharp changes of up to 1°C over distances of less than 0.5 nm (Figure 5.6-b). Salinity varied from 35.2 to 35.3 (Figure 5.6-c), but as for $\theta_0$ displayed very sharp changes over short distances. Chlorophyll $\alpha$ concentrations, $c(\text{chlo-}\alpha)$, (Figure 5.6-d) in surface waters ranged from 0.1 to 4 mg m$^{-3}$ and were on average 1.33±0.78 mg m$^{-3}$. The $c(\text{chlo-}\alpha)$ also presents high variability, in particular between year-day 127 up to year-day 135.

![Figure 5.6: Calibrated O2 concentrations (c(O2)), sea surface temperature (\theta_0), salinity and chlorophyll-a concentration (c(chlo-a)) in surface waters over time (year-day).](image)

Mixed layer depths ($z_{\text{mix}}$) are relatively deep (78 m) at the beginning of the cruise. This is probably associated with a storm on year-day 124 (3 May 2008), which shows as a high $k_w$ on
year-day 127 (Figure 5.7). After this storm event, the water column appears more stratified, with $z_{\text{mix}}$ ranging from 10 to 66 m until the end of the cruise.

![Figure 5.7](image_url)  
**Figure 5.7:** Weighted gas transfer coefficient calculated after Reuer et al. (2007) which integrates wind speeds from 60 days previous to the measurements. Wind speed data was extracted from the cross-calibrated multi-platform, CCMP, wind product reanalysis (Atlas et al., 2009).

### 5.3.1. Net community production from continuous $O_2$ measurements and discrete $O_2/Ar$.

The oxygen saturation anomaly was $6.3 \pm 2.5\%$ (Figure 5.8) during the cruise with values ranging from 1.1% to 13.7%. Its spatial variability was high, similar to the $c(O_2)$, with changes of up to 4% over just 0.4 nm distances, as for example on 17 May (year-day 138, Figure 5.8). These sharp changes can also be observed in the centre of the grid between 27° W to 25.7° W and 61.2° N to 61.6° N (Figure 5.9). Removal of the physical effect as given by $\Delta(Ar)$ (using equation 5.5) provides a mean $\Delta(O_2/Ar)$ of 5.93%.

![Figure 5.8](image_url)  
**Figure 5.8:** Oxygen saturation anomaly, $\Delta(O_2)$, in surface waters over time. Note the rapid changes in $\Delta(O_2)$.  

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The **vertical diffusive flux** \( (F_v) \) (equation 5.2) is presented in Figure 5.10, with positive fluxes indicating diffusive mixing of \( \text{O}_2 \) into the mixed layer and negative fluxes indicating diffusion of \( \text{O}_2 \) out of the mixed layer. Overall the flux was negative, meaning diffusion of \( \text{O}_2 \) from the mixed layer to the water below. The mean diffusive flux was \(-2.41\pm4.06 \text{ mmol m}^{-2} \text{ d}^{-1}\).

Figure 5.9: The oxygen saturation anomaly, \( \Delta(\text{O}_2) \), in surface waters. Colour indicates the \( \Delta(\text{O}_2) \). The top panel represents \( \Delta(\text{O}_2) \) of all data collected, and the bottom panel is the inset of the area inside the box in the top panel.
Figure 5.10: The vertical diffusive flux of $O_2$ calculated using the gradient of $O_2$ between the bottom of the mixed layer and a depth 10 m below the $z_{mix}$ and a $k_v$ of $10^{-4}$ m d$^{-1}$. Positive fluxes indicate diffusive mixing of $O_2$ into the mixed layer from waters below, negative fluxes indicate a loss by diffusion from the mixed layer to the deeper layers.

Taking into account respiration in the ship’s pipes, the physical contribution on $\Delta(O_2)$ and the losses of $O_2$ by vertical diffusion to the waters below is calculated a $N(O_2/Ar)$ of 48.5±18.1 mmol m$^{-2}$ d$^{-1}$ with equation 5.7. For this estimate horizontal mixing was neglected. This would not be very realistic for individual data points in the light of the large spatial variability in the other parameters, for example ($\Delta(O_2)$, $\theta_0$, $S_0$, $c$(chlo-a)). However, since horizontal mixing influences cancel out for this spatial average value, in this study was nevertheless considered to be representative for the biological community in the region of interest.

A similar value of $N_{\text{discrete}}$ ($O_2/Ar$) of 56.0±16.6 mmol m$^{-2}$ d$^{-1}$ is obtained, if only the discrete $O_2/Ar$ data from the evacuated bottles are used and a correction is made for the respiration in the pipes.

5.3.2. Net community production for the water mass identified by the Lagrangian float

The spatial heterogeneity for $\theta_0$, $S_0$ and other parameters in this region (Figure 5.6), challenges the assumption of steady state, which is necessary for $N(O_2/Ar)$ to fully represent net community production. For the assumption of steady state to be true, the calculation of $N(O_2/Ar)$ was repeated for the NAB’08 bloom waters, as identified by the Lagrangian float (Alkire et al., 2012). This float surfaced every day, which provided a daily location which was
used as a proxy to identify the same water mass. Thus for this analysis it was considered only data that was within a distance $d$ from the float. The distance $d$ was defined as the minimum distance at which a sharp change in the $\Delta(O_2)$ values occurred. The value of “$d$” was observed to be 0.4 nm with a change of 3.9% in the $\Delta(O_2)$ on year-day 138.42, or 07 May 10:14 (Figure 5.8). In practice most data with $d$ smaller than 0.4 nm were only observed when the float surfaced (Figure 5.12).

The data within distance “$d$” always presented high values of $\Delta(O_2)$, which indicates that these points were in an area inside the bloom. $\Delta(O_2)$ values ranged from 7 to 12% and were of 9%±1% on average, resulting in an $N(O_2/Ar)$ of 67.2±23.3 mmol m$^{-2}$ d$^{-1}$.

None of the discrete $O_2/Ar$ collection times corresponded to a distance of less than 0.4 nm; therefore, only continuous $O_2$ data could be used.

![Figure 5.11: $\Delta(O_2)$ over time (year-day) for the data within 0.4 nm of the float-track. The data here represents the averages, with standard deviation as the error bars, of each of the periods when the float surfaced.](image)

### 5.3.3. Comparison to Paul Quay’s findings

Six discrete samples were taken in duplicate in 6 different locations for an intercomparison of isotopic and $O_2/Ar$ analyses by the laboratories of Paul Quay and UEA. A comparison of $\Delta(O_2/Ar)$ values from these discrete samples resulted in a mean of the differences of $\Delta(O_2/Ar) = 0.30±0.41$ % (Table 5.1, average±standard deviation). This standard deviation is smaller than the standard deviation of this study samples replicates (0.36%) and of
those analysed by Paul Quay (0.76%), suggesting agreement between the two sets of analyses for Δ(O₂/Ar).

There is not such agreement between the analyses of the isotopic compositions of these two groups of samples: The difference between this study samples and Quay’s samples for $^{17}\delta$ and $^{18}\delta$ was 0.542±0.042 ppm and 0.997±0.076 ppm, respectively. These differences are much greater than the mean standard deviation of the measurements by either Paul Quay or the present study, with highest values of 0.085 and 0.163 for $^{17}\delta$ and $^{18}\delta$, respectively, for the analyses by Paul Quay. For $^{17}\Delta$, the mean difference of this study samples minus Quay’s is 25±24 ppm, which is twice the standard deviation of samples analysed by Quay and similar to the standard deviation for the present study samples. Therefore, although the difference of the Δ(O₂/Ar) analyses by the two laboratories is not significant, the analyses of the isotopic compositions are different.

![Figure 5.12: The oxygen concentration in surface water over time. Black points represent all available data, and red points represent data within 0.4 nm of the float-track. Black lines represent the timings at which the float was surfacing.](image)

<table>
<thead>
<tr>
<th>[UEA-Quay] mean ± stdev</th>
<th>$\Delta$(O₂/Ar) (ppm)</th>
<th>$^{17}\delta$ (%)</th>
<th>$^{18}\delta$ (%)</th>
<th>$^{17}\Delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quay's stdev</td>
<td>0.76%</td>
<td>0.085</td>
<td>0.163</td>
<td>11</td>
</tr>
<tr>
<td>UEA's stdev</td>
<td>0.36%</td>
<td>0.013</td>
<td>0.071</td>
<td>22</td>
</tr>
</tbody>
</table>

**Table 5.1:** Summary of the results of a comparison of 7 seawater samples. In the first row is presented the mean ± standard deviation of the difference between this study data (UEA) and Paul Quay’s. The second and third row shows the mean standard deviation of the samples by Paul Quay and UEA, respectively.
5.3.4. Gross O₂ production in the North Atlantic Bloom

Calculation of the gross oxygen production was done from the discrete evacuated bottle samples collected from the USW and the surface CTD. From them it was obtained a $g_{KA}$ of 0.8±1.3 which resulted in an average gross oxygen production $G_{KA}$ of 542±804 mmol m⁻² d⁻¹, if the $\delta^{15}$SMOW (where “i” is 17 or 18) as reported by Kaiser and Abe (2012) is used. For the $\delta^{18}$SMOW as reported by Barkan and Luz (2011) it was obtained a $g_{BL}$ of 0.4±0.5 and a $G_{LB}$ of 304±316 mmol m⁻² d⁻¹. Calculating the f ratio as $f = \Delta(O_2/Ar)/g$ (Bender, 2000) it was obtained a $f_{KA}$ 29% and $f_{BL}$ 39%.

5.4. Discussion

(1) Several surface water parameters, temperature, salinity, c(chlo-a), c(O₂) and $\Delta$(O₂) — showed high variability with very sharp changes across small distances. This variability was expected, as earlier studies had described the heterogeneity of this area with its scattered submesoscale eddies.

(2) From continuous surface measurements of c(O₂), discrete measurements of $\Delta$(Ar) and estimates of air-sea exchange of O₂, here is reported a first-order (first order because horizontal mixing is ignored) estimate of $N_{cont}(O_2/Ar)$ for this area of 48.5±18.1 mmol m⁻² d⁻¹ and a first-order estimate $N_{discrete}(O_2/Ar)$ from the discrete O₂/Ar data of 55.0±16.6 mmol m⁻² d⁻¹. $N_{discrete}(O_2/Ar)$ estimates from the discrete bottles were higher than those of the continuous data. This difference was expected because $N_{cont}(O_2/Ar)$ included regions of lower productivity like the leg South of 60.6° N where $\Delta$(O₂) were much smaller than the central area where all the discrete samples of O₂/Ar were collected (Figure 5.9). This is also evident from the larger standard deviation for the continuous measurements of 18.1 mmol m⁻² d⁻¹, relative to 16.6 mmol m⁻² d⁻¹ for the discrete measurements.

(3) Based on a set of 32 samples collected from the same 3-week bloom study, Paul Quay reported a mean $N(O_2/Ar)$ of 87±12 mmol m⁻² d⁻¹ (Quay et al., 2012). Using his raw data, it was obtained a mean of 55.0±16.6 mmol m⁻² d⁻¹. Quay et al. (2012) and this study used the same wind speed parameterization (Nightingale et al., 2000); therefore this difference could only be explained by the different approach to calculating $z_{mix}$ used for the calculation of $k_w$ (Reuer et al., 2007), and the different wind data product used for the calculation of $k$. Quay et al. (2012) defined their $z_{mix}$ by a difference of 0.03 kg m⁻³ relative to 10 m depth; in this study was used a difference of 0.01 kg m⁻³ because this criterion seemed to correspond more closely.
to the changes in \(O_2\) in the water column. Moreover, others have used this same criterion (Alkire et al., 2012). The effect of the choice of \(z_{\text{mix}}\) criterion on \(N\) was tested and that it was found to represent 9% of the value of \(N(O_2/Ar)\).

The other parameter that differed between the two estimates of \(N\) was the wind speed product used to calculate \(k_w\). While Quay et al. (2012) used QuickSCAT data for which he reported a difference of 1 m s\(^{-1}\) from buoy data, for the present study it was used cross calibrated multi-platform, CCMP (Atlas et al., 2009) wind product, which differed from the ship’s wind speed by 1 m s\(^{-1}\). Using only the data of this study, it was calculated that a change of \(\pm 2\) m s\(^{-1}\) in the wind speed would cause \(N(O_2/Ar)\) to vary by as much as \(\pm 50\%\).

Both the mixed layer depth \(z_{\text{mix}}\) and the choice of wind speed product, affect the calculation of \(N\). The different assumptions for \(z_{\text{mix}}\) and the wind speed product, or just the choice of wind speed alone can explain the difference between the \(N\) values reported by Quay et al. (2012) and UEA. If \(N(O_2/Ar)\) is calculated for Quay’s samples for the same parameters that were used for treating the data of this study it was obtained: \(N(O_2/Ar, \text{Quay}) = 55.0 \pm 16.8\) mmol m\(^{-2}\) d\(^{-1}\). This value is very close to this study from 53 bottles: \(N_{\text{discrete}}(O_2/Ar, \text{UEA}) = 56.0 \pm 16.6\) mmol m\(^{-2}\) d\(^{-1}\). Combining the results from the discrete samples by Quay and UEA, \(N_{\text{discrete}}(O_2/Ar) = 55.6 \pm 16.6\) mmol m\(^{-2}\) d\(^{-1}\) is obtained.

(4) The laboratory intercomparison (Table 5.1) has shown that \(\Delta(O_2/Ar)\) for both Quay and myself are very similar. This is not the case for the \(^{17}\delta\) and \(^{18}\delta\). The higher values of this study samples are due most likely to a mass dependent fractionation of the samples, which results in removal of the lighter isotopes and leaving behind the heavier molecules. But this cannot be the only explanation as if it was only mass dependant fractionation \(G\) would be not so affected. Probably some error while transferring the samples might have occurred.

(5) Given the heterogeneity of this region, it would be more correct to give an individual \(N\) value for each of the different water masses. By studying the same water mass, it can be assumed steady state. When using only the data that was within the same water as the Lagrangian float, which is considered to be always in the same water mass, a \(N(O_2/Ar)\) of 67.2 \pm 23.3 mmol m\(^{-2}\) d\(^{-1}\) was found. This value was higher than the earlier \(N_{\text{cont}}(O_2/Ar)\) of 43.46 \pm 17.82 mmol m\(^{-2}\) d\(^{-1}\) and \(N_{\text{discrete}}(O_2/Ar)\) of 55.6 \pm 16.6 mmol m\(^{-2}\) d\(^{-1}\). A higher value for \(N\) in the productive bloom waters than for the region as a whole is expected, as relatively high values of \(\Delta(O_2)\) and \(c(O_2)\) were also found in the patch of water identified by the float (Figure 5.12 and Figure 5.13).
When examined only the data collected from the water mass in close proximity (0.4 nm) to the float, I obtained a value for \( N(O_2 / Ar) \) of \( 67.2 \pm 23.3 \text{ mmol m}^{-2} \text{ d}^{-1} \). This estimate was higher than two previous estimates by 31% and 18%, generated from continuous and discrete samples, respectively. This higher value is attributed to the distinctively higher production, indicated by higher concentrations of \( O_2 \) (Figure 5.12 and Figure 5.13) in the water mass nearest to the float than that in neighbouring water masses.

**Figure 5.13:** Density as calculated from \( \theta_a \) and salinity measured in the surface waters versus time. Coloured points represent the \( c(O_2) \). Areas in black denote locations where \( O_2 \) data is unavailable. The data points between the vertical, closely spaced red lines depict data within 0.4 nm of the float used for the analysis of \( N \) by means of an oxygen budget \( N(O_2 \text{ budget}) \). Horizontal black dashed lines depict the density limits of the data analyzed for the study of \( N(O_2 \text{ budget}) \).

The water mass, which the float was following, had a relatively low density and was warmer than the neighbouring water masses (Figure 5.13). This may indicate that the warmer, more strongly stratified waters enabled the development of the bloom (Mahadevan et al., 2012).

Observing the data obtained close to the float over time, the \( O_2 \) concentration increases from 300 \( \mu \text{mol kg}^{-1} \) to 312 \( \mu \text{mol kg}^{-1} \) over a 6-day period (year-day 128.7-134.7), then decreases again to its initial values of around 300 \( \mu \text{mol kg}^{-1} \) over a 5-day period (year-day 134.7-139.7, Figure 5.12). This tendency was also shown by Alkire et al. (2012) for the data acquired with the float. They studied the bloom dynamics over time with budget calculations of \( O_2 \), \( NO_3^- \) and particulate organic carbon (POC). Based on the \( O_2 \) budgets, they separated the bloom into several stages and calculated net community production (in terms of \( O_2 \) and using a \( PQ=1.45 \), as they report in the paper): an early bloom (96±51 mmol m\(^{-2}\) d\(^{-1}\)); the main bloom
(167±74 mmol m⁻² d⁻¹); the termination (-270±120 mmol m⁻² d⁻¹) and post-bloom (3±32 mmol m⁻² d⁻¹). The ship was on location only for the main bloom and the early stages of the post-bloom.

Below is calculated net community production based on O₂ budgets in the mixed layer for short periods of several days. These N values for short periods differ from my previous estimates of N (N_{conv}(O₂/Ar), N_{discrete}(O₂/Ar), which integrate relatively long time periods of several weeks. Here it will be N estimates based on O₂ budgets in the mixed layer with the float estimates of N by Alkire et al. (2012) for the main bloom and the early stages of the post-bloom.

Net community production based on O₂ budgets was calculated as the change over time of the c(O₂) inventory (I, mmol m⁻³) in the mixed layer accounting for air-sea gas exchange:

\[
I_{(i)} = \int_{0}^{z_{\text{mix}}} c_{(i)}(O_2) \, dz = c_{(i)}(O_2) \, z_{\text{mix}} \tag{5.10}
\]

\[
F_{\text{ASE}(i)} = k_{w(i)} \left[ c_{(i)}(O_2) - c_{\text{sat}(i)}(O_2) \right] \tag{5.11}
\]

\[
N(\text{O}_2 \text{ budget}) = \frac{I_{(i+1)} - I_{(i)}}{t_{(i+1)} - t_{(i)}} + \frac{(F_{\text{ASE}(i)} + F_{\text{ASE}(i+1)})}{2} \tag{5.12}
\]

Where \( I_{(i)} \) is the inventory in the mixed layer at the time \( i \), \( c_{(i)}(O_2) \) is the concentration of O₂ at time \( i \), \( z_{\text{mix}} \) is the mixed layer depth, \( c_{\text{sat}(i)}(O_2) \) is the saturation concentration of O₂ at time \( i \), \( F_{\text{ASE}(i)} \) is the air sea flux at time \( i \) and \( k_{w(i)} \) the weighted gas transfer coefficient at the time \( i \). \( z_{\text{mix}} \) was of 18±5 m which was the mean of the \( z_{\text{mix}} \) of the data within 0.4 nm of the float. The results, obtained using this approach, are presented in Figure 5.14 versus time. Only data points within 0.4 nm radius of the float were used.
Figure 5.14: Net community production based on O$_2$ budget for the mixed layer, N(O$_2$ budget), over time. The width of the columns represents the time for which they were integrated. In grey circles, triangles and crosses are the total carbon biomass of microphytoplankton, nanophytoplankton and total heterotrophic organisms (nanoflagellates and bacteria), respectively.

$N(O_2$ budget) shows a change over time, with prevailing net autotrophy (positive $N$) between year-days 128.7 and 134.7 with values starting at 60 mmol m$^{-2}$ d$^{-1}$ and reaching 170 mmol m$^{-2}$ d$^{-1}$. For about 2 days from day 134.7 net heterotrophy dominates, presenting values of -10 and -42 mmol m$^{-2}$ d$^{-1}$. After that period, the $N(O_2$ budget) increased to positive values (net autotrophy) of 18 and 5 mmol m$^{-2}$ d$^{-1}$. The net autotrophy prevails for the rest of the sampling period.

Alkire et al. (2012) found a similar pattern, with high values for $N$ of from year-days 127-134 and a sudden decrease occurring between year-day 134 and 135, which matches our overall trend.

(6) Here are compared the estimates from this study to those of Alkire et al. (2012), using only Alkire et al.’s $N(O_2$ budget) time span, which extends from year-day 127 to 135. Alkire et al.’s $N(O_2$ budget) for the Main Bloom (year-days 127 to 134) is 115±51 mmol m$^{-2}$ d$^{-1}$, which corresponds to this study budget calculations from day 128.7 to 134.7, during which $N$ was 111±56 mmol m$^{-2}$ d$^{-1}$ (ranging 60 to 170 mmol m$^{-2}$ d$^{-1}$). The “Termination” stage defined by Alkire et al. (year-day 134-135) is characterized by a high heterotrophic event with a $N(O_2$ budget) of -186±83 mmol m$^{-2}$ d$^{-1}$. Although this study did not find such a low $N(O_2$ budget), it did find a corresponding net heterotrophic event between year-days 134.7-136.7 with an
initial value for $N$ of $-10$ mmol m$^{-2}$ d$^{-1}$ that decreased to $-42$ mmol m$^{-2}$ d$^{-1}$ on the second day. After this period of net heterotrophy (after year-day 136.7), a new period started characterised by a low net autotrophy that was nearly in metabolic balance with values of 18 and 5 mmol m$^{-2}$ d$^{-1}$. However, Alkire et al. (2012) do not present data for this period as they encounter a different water mass from a cold core eddy, but because this eddy does not appear in surface waters (which are the focus of this study) this period is included (Figure 5.13).

(7) Associated with the changes in $N$(O$_2$ budget) were the changes in the plankton communities. Measurements of chlorophyll-a concentration -c(chlo-a)- (Figure 5.15) and species abundance (Figure 5.14) from the USW followed a very similar pattern to the $N$(O$_2$ budget) with the highest values between year-days 131.7 until 133.7. The minimum at year-day 136.7 matched the period of net heterotrophy. Afterwards as the $N$(O$_2$ budget) increases, the c(chlo-a) also increases slightly.

![Figure 5.15: USW chlorophyll a concentration, c(chlo-a), at the locations within 0.4 nm of the float. Bars represent the standard deviation of data for each timing.](image)

Species abundance samples were collected at selected stations by Mike Sieracki and Nicole Poulton (Bigelow Laboratory for Ocean Science) and analyzed with a Becton Dickinson FACScan flow cytometer (Sieracki and Poulton, 2011). The samples were used for estimating the biomass of microphytoplankton (sum of autotrophic groups: diatom, dinoflagellates, ciliates and other chlorophyll containing particles), nanophytoplankton (including photosynthetic picoeukaryotes, Synechococcus and cryptophytes) and the heterotrophic (bacteria and nanoflagellates) organisms within the mixed layer. Four of these stations with plankton abundance data matched the location of the float surfacing (Figure 5.14). The net
autotrophic event between year-days 128.7 and 134.7 coincided with a high carbon (C) abundance of microphytoplankton. The C biomass of these groups of over 100 µg l⁻¹ on year-day 132.7 sharply declined during and after the heterotrophic period to 40 and 19 µg l⁻¹. The opposite happened to the carbon biomass of nanphytoplankton, which started at 26 µg l⁻¹ and steadily increased to 62 µg l⁻¹ at the last station on day 137.7. The biomass of the heterotrophic community started at 17 µg l⁻¹ at the first station on year day 128.7 and increased to 29-27 µg l⁻¹ at the last two stations. The change in species composition is of special relevance, as has been described earlier (Sieracki et al., 1993) and for this bloom (Briggs et al., 2011; Martin et al., 2011), because the shift from diatoms to smaller phytoplankton (due to the depletion of Si), is generally associated with a high export event to depth. Such export events dominate the annually integrated carbon export, but part of the exported carbon is respired and returned to the atmosphere when the mixed layer deepens in winter. (Körtzinger et al., 2008; Quay et al., 2012).

(8) Estimates of $G$ either using the $\delta_{SMOW}$ as reported by Kaiser and Abe (2012) or Barkan and Luz (2011) were much higher than values calculated from the measurements of Quay et al. (2012) which gave a $G_{\text{ KA}}$ of 171±80 mmol m⁻² d⁻¹ or $G_{\text{ LB}}$ of 124±57 mmol m⁻² d⁻¹. Values when using Kaiser and Abe were 3.2 times higher than those of Quay et al. (2012) and when using the Barkan and Luz the values were 2.5 times higher. Quay et al. (2012) reported $f$ values of 0.40, but when calculated the $f$ ratio from their values I obtained 0.40-0.54, which is considerably larger than the $f$ ratio for this present study data of 0.29-0.39.

5.5. Conclusions

(1) The North Atlantic in Bloom presents very high variability which shows in the $\theta_{0}$, salinity, $c$(chlo-a) and $c$(O₂) with sharp changes over distances of 0.4 nm. This high variability was due to crossing different water masses as shown by the data. It is probable that the different water masses are at different stages of the spring bloom.

(2) When not considering the spatial variability it was calculated a first order $N$ that ranges 48.5-56 mmol m⁻² d⁻¹ from continuous and discrete measurements, respectively. The $N$ of 56 mmol m⁻² d⁻¹ as measured by the discrete samples analyzed at UEA compared very well with the $N$ value calculated with the data from Quay et al. (2012) of 55±16.8 mmol m⁻² d⁻¹, for the same wind speed product and $z_{\text{mix}}$. 

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(3) The selection of the wind speed product is highly relevant for the calculation of $N$. A different wind speed product might explain why the data reported by Quay et al. (2012) of 87 mmol m$^{-2}$ d$^{-1}$ differ so strongly from the value of 55±16.8 mmol m$^{-2}$ d$^{-1}$, that I calculate when using his O$_2$/Ar data.

(4) Net community production in the water mass with the bloom, as identified by the float, is as high as 67.3 mmol m$^{-2}$ d$^{-1}$. This is considerably higher than the regional estimate of 48.5-56 mmol m$^{-2}$ d$^{-1}$ from continuous and discrete measurements. This highlights the relevance of submesoscale studies of bloom evolution.

(5) Seven replicate samples were analyzed independently as a laboratory intercomparison for their $\Delta$(O$_2$/Ar), $^{17}\delta$ and $^{18}\delta$ in Paul Quay’s laboratory and in Jan Kaiser’s laboratory at UEA. The $\Delta$(O$_2$/Ar) ratios were similar, but values for $^{17}\delta$ and $^{18}\delta$ differed considerably between the two laboratories.

(6) When looking at the evolution of O$_2$ within one water mass, as identified by a Lagrangian float, it was observed a similar development as Alkire et al. (2012). High values of net community production, as high as 170 mmol m$^{-2}$ d$^{-1}$, were followed by a short period of net heterotrophy, before returning to net autotrophy but with lower values than before and not as high as previously when dominated by microphytoplankton (mainly diatoms). This is especially relevant because diatoms are important triggers of ocean carbon export to deeper layers when stressed by silica depletion.
Chapter 6. Conclusions and future work
6.1. Conclusions

The aim of this research was to estimate marine biological production in two distinct areas of the Atlantic Ocean: In the subpolar north Atlantic spring bloom and in the oligotrophic gyre of the South Atlantic. Mixed-layer net community production \((N)\) and gross oxygen production \((G)\) were estimated by continuous measurements of \(\text{O}_2/\text{Ar}\) and discrete analyses of \(\text{O}_2\) isotopologues, respectively.

For the purpose of measuring \(G\) an automated extraction line was built for the analysis of the isotopic composition of \(\text{O}_2\) dissolved in sea water. This was a joint undertaking between another PhD student (Johanna Gloël). This facility is the first of its kinds in Europe and is currently being used for samples from other regions such as the Southern Ocean.

Measurements of \(N\) and \(G\) in these two areas of the Atlantic Ocean are of relevance for the biological marine carbon cycle. The North Atlantic is thought to account for 23 % of the total anthropogenic carbon (C) uptake by the oceans (Sabine et al., 2004), due to the high biological activity (in particular during spring blooms) together with enhanced physical gas transfer due to cooling of surface waters. In contrast, it is being debated whether the South Atlantic gyre is net autotrophic (i.e. a net carbon sink) or net heterotrophic (i.e. a net carbon source) (Duarte et al., 2013; Ducklow and Doney, 2013; Williams et al., 2013). The metabolic state of oligotrophic gyres is of relevance for the global marine carbon cycle because of their sheer size.

The results from a cruise in the South Atlantic gyre in austral autumn of 2009 showed consistent net autotrophy for the gyre with net community \(\text{O}_2\) production of \((10 \pm 3)\) mmol m\(^{-2}\) d\(^{-1}\) which contrasts with previous measurements by means of bottle incubations that found lower net production and often net heterotrophy (Gist et al., 2009; González et al., 2002; Serret et al., 2006). Net community production measurements using \(\text{O}_2/\text{Ar}\) ratios in different gyres showed agreement with our estimates (Juranek et al., 2012; Luz and Barkan, 2009; Quay et al., 2010). It is true that the techniques used here only considered the production in the mixed layer compared to in vitro estimates that integrate over the whole mixed layer. This applies to both \(N\) and \(G\). So, actually, what might be perceived as a bias (i.e. the flux of \(\text{O}_2\) and \(^{17}\text{O}\) excess from the upper thermocline into the mixed layer in the gyres) actually just offsets the error made by considering only the mixed layer rather than the entire productive region. Therefore \textit{in situ} measurements using continuous \(\text{O}_2/\text{Ar}\) data confirm that the South Atlantic was net autotrophic at the time of sampling.
The source of nutrients to the gyre is discussed in relation to measurements of N₂ fixation rates and δ¹⁵N, PON) from Mark More. It seems that there are two distinct regions within the gyre. West of 10° W, N₂ fixation dominates and NO₃ based production is dominant east of 10° W. This is relevant to determine what sustains the observed net autotrophy.

Measurements of G in the gyre show high rates of (177±98) mmol m⁻² d⁻¹ when using the isotope delta of mean seawater relative to atmospheric oxygen (δVSMOW) of Kaiser and Abe (2012). With the corresponding isotope delta of Luz and Barkan (2011) (122±63) mmol m⁻² d⁻¹ was obtained. Both of these estimates are higher (by at least a factor of two) compared to previous studies in this area made by ¹⁴C or O₂ light and dark bottle incubations (Gist et al., 2009; Marañón et al., 2003; Serret et al., 2006). There could be several reasons for this including problems related to bottle incubation methods, which would underestimate gross oxygen production measured with the O₂ light and dark incubation method and primary production derived from ¹⁴C measurements. Problems that could lead to overestimation of G are the uncertainty in the gas transfer coefficient, entrainment of O₂ from below the mixed layer and processes that might mask the G like the Mehler reaction which produces an anomaly in the isotopic composition of the O₂ pool, but does not fix carbon. It was hypothesized that high values of Fᵥ/Fₘ found in the gyre were indicative of the Mehler reaction playing an important role in this region of the Atlantic. Its contribution to gross O₂ production may be higher than the 15 % that are usually assumed (Bender et al., 1999). The Mehler reaction induced by light and nutrient stress (Grossman et al., 2010) may therefore have led to higher values of G compared to other studies.

The measurements of G agree well with other studies using O₂ isotopologues in the North Pacific and North Atlantic gyres (Juranek and Quay, 2010; Juranek et al., 2012; Quay et al., 2010).

The second case study was performed during a cruise south of Iceland that studied the North Atlantic Bloom. The surface water showed very high spatial variability in temperature, salinity and oxygen concentrations. This variability is attributed to different water masses, which are interpreted to be in different stages of the bloom. If this variability is ignored, then N was estimated to be of 48.5 and 56 mmol m⁻² d⁻¹ from continuous O₂ measurements and discrete O₂/Ar ratio measurements, respectively.

During the cruise, a water parcel was tracked by a Lagrangian float, which was followed over a period of 11 days. The surrounding water parcel was in close proximity to the
float was considered to be in the bloom phase because of the higher $\Delta(O_2)$ in comparison to surrounding waters and $N$ was on average of 67 mmol m$^{-2}$ d$^{-1}$. Over time an evolution in the $O_2$ concentration was observed similar to that of Alkire et al. (2012) who used $O_2$ measurements on the float directly. Associated with it were changes in the community structure as well as the concentration of chlorophyll.

During the cruise samples were collected for another group led by Paul Quay who also performed production measurements using discrete analyses of $O_2$ isotopologues and $O_2$/Ar ratios. Their published results differ from mine because they used a different wind speed product to calculate the gas transfer coefficient. When using the same wind speed product our measurements agreed well. This highlights the systematic uncertainties of the method due to parameterisation of the air-sea gas exchange rates.

During both cruises a change of $O_2$ concentrations from in situ values (measured in CTD samples) to the point of sampling inside the ship, after the water had been pumped through the ship's pipes. This was $-0.87 \mu$mol kg$^{-1}$ for the North Atlantic cruise, which resulted in a net decrease of 0.3 %, and $-0.91 \mu$mol kg$^{-1}$ corresponding to a net decrease of 0.5% for the South Atlantic cruise (see Chapter 4). This is slightly lower than values reported by Juranek et al. (2010), which ranged from 1 $\mu$mol kg$^{-1}$ to 4 $\mu$mol kg$^{-1}$, indicating that cleaning of the pipes that took place before the cruises may have had a positive effect.

### 6.2. Future research

Measurements of $\Delta(O_2$/Ar) and oxygen isotopes are used more and more widely. These methods have the advantage that they can measure in situ and that their sampling requirements are less laborious than incubation methods. For instance, $\Delta(O_2$/Ar) ratios can be measured at rates as high as 10 s with precisions up to 0.1% (other authors have done better and achieved $<0.05\%$) using atmosphere-equilibrated water as a standard; for $O_2$ isotopologues, samples can be collected and kept for future analysis.

To improve these methods it is important to reduce the uncertainty of the following parameters: For both $N$ and $G$ estimates, it is relevant to have a (1) better knowledge of the gas transfer coefficient as currently as this is one of the major sources of error in $N$ and $G$. Also using the appropriate wind speed products can considerably change $N$ and $G$. 

Then, specifically concerning only to $G$, it is important that more work is done to understand the nature of the gross production rates measured with this technique in relation to "conventional" estimates, e.g. using $^{14}$C incubations and to improve the accuracy of the underlying isotopic parameters: (2) Independent determinations of $\delta_{\text{VSMOW}}$ could help determine their true value and thus more accurate calculations of $G$. (3) Better knowledge of the extent of processes that might mask $O_2$ production such as the Mehler reaction. (4) More measurements of the fractionation of $O_2$ by photosynthesis for different species as currently there are only 5 species for which this is known. (5) More experiments to determine $\delta_{\text{sat}}$.

At the locations of study, it was demonstrated that the measurement of $O_2/Ar$ ratios in the gyres can determine $N$ but more measurements need to be done in order to determine annual rates and interannual changes. Also, continuous measurements of $O_2/Ar$ ratios are a powerful tool for dynamical regions like the North Atlantic Bloom.

It is true that the techniques used here only considered the production in the surface mixed layer compared to in vitro estimates that can integrate over the whole euphotic zone. This applies to both $N$ and $G$. So, actually, what might be perceived as a bias (i.e. the flux of $O_2$ and $^{17}$O excess from the upper thermocline into the mixed layer in the gyres) actually just offsets the error made by considering only the mixed layer rather than the entire productive region.


University of Southampton, p. 173.


Steeman Nielsen, E., 1952. The use of radiative carbon (C$_{14}$) for measuring organic production in the sea. Journal Pour la Conseil International d'Exploration de la Mer 18 (2), 117-140.


### Glossary

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\gamma_r$</td>
<td>Ratio of $^{17}$O/$^{16}$O isotopic fractionation to $^{18}$O/$^{16}$O isotopic fractionation during respiration, calculated as $^{17}\varepsilon_r / ^{18}\varepsilon_r$</td>
</tr>
<tr>
<td>$\theta_o$</td>
<td>Sea surface temperature</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Relative isotope ratio difference</td>
</tr>
<tr>
<td>$^{17}\delta_p, ^{18}\delta_p$</td>
<td>Relative isotope ratio difference of biologically produced O$_2$</td>
</tr>
<tr>
<td>$^{17}\delta_{sat, ^{16}}^{18}\delta_{sat}$</td>
<td>Relative isotope ratio difference of dissolved O$_2$ in equilibrium with the atmosphere</td>
</tr>
<tr>
<td>$^{17}\delta_{VSMOW, ^{16}}^{18}\delta_{VSMOW}$</td>
<td>Relative isotope ratio difference of VSMOW compared to atmospheric O$_2$</td>
</tr>
<tr>
<td>$^{17}\delta_{W, ^{16}}^{18}\delta_{W}$</td>
<td>Relative isotope ratio difference of water compared to atmospheric O$_2$</td>
</tr>
<tr>
<td>$\delta(N_2/O_2)$</td>
<td>Relative N$_2$/O$_2$ gas ratio difference between two samples</td>
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<tr>
<td>$\delta(O_2/Ar)$</td>
<td>Relative O$_2$/Ar gas ratio difference between two samples</td>
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<tr>
<td>$\Delta(O_2/Ar)$</td>
<td>Biological oxygen saturation anomaly</td>
</tr>
<tr>
<td>$\Delta(Ar)$</td>
<td>Ar saturation anomaly</td>
</tr>
<tr>
<td>$\Delta(O_2)$</td>
<td>O$_2$ saturation anomaly</td>
</tr>
<tr>
<td>$^{17}\Delta$</td>
<td>$^{17}$O excess, defined as equation 1.7</td>
</tr>
<tr>
<td>$^{17}\Delta_{sat}$</td>
<td>$^{17}$O of O$<em>2$ in equilibrium with the atmosphere and calculated from $^{17}\delta</em>{sat}$ and $^{18}\delta_{sat}$</td>
</tr>
<tr>
<td>$^{17}\Delta_p$</td>
<td>$^{17}$O of biologically produced O$_2$ calculated from $^{17}\delta_p$ and $^{18}\delta_p$</td>
</tr>
<tr>
<td>$^{17}\varepsilon_E, ^{18}\varepsilon_E$</td>
<td>Isotopic fractionation during evasion of O$_2$ from water to atmosphere</td>
</tr>
<tr>
<td>$^{17}\varepsilon_i, ^{18}\varepsilon_i$</td>
<td>Isotopic fractionation during invasion of O$_2$ from atmosphere into water</td>
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<tr>
<td>$^{17}\varepsilon_p, ^{18}\varepsilon_p$</td>
<td>Isotopic fractionation during photosynthesis</td>
</tr>
<tr>
<td>$^{17}\varepsilon_R, ^{18}\varepsilon_R$</td>
<td>Isotopic fractionation during respiration</td>
</tr>
<tr>
<td>$c(\text{chlo-}a)$</td>
<td>Chlorophyll a concentration</td>
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<tr>
<td>$c(O_2), c(Ar)$</td>
<td>Concentration of dissolved O$_2$ and Ar in water</td>
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<tr>
<td>$c_{sat}(O_2), c_{sat}(Ar)$</td>
<td>Saturation concentration of O$_2$ and Ar in water</td>
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<tr>
<td>$f$</td>
<td>Ratio of net community oxygen production to gross oxygen production ($N/G$)</td>
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<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>$F_{\text{Bio}}$</td>
<td>Biological O$_2$ air-sea flux</td>
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<tr>
<td>FRRF</td>
<td>Fast repetition rate fluorometer</td>
</tr>
<tr>
<td>G</td>
<td>Gross oxygen production, determined with triple oxygen isotope method</td>
</tr>
<tr>
<td>g</td>
<td>Ratio of gross production G to gas exchange</td>
</tr>
<tr>
<td>IRMS</td>
<td>Isotope ratio mass spectrometer</td>
</tr>
<tr>
<td>k</td>
<td>Gas exchange coefficient</td>
</tr>
<tr>
<td>$k_w$</td>
<td>Weighted gas exchange coefficient, adapted after Reuer et al. (2007)</td>
</tr>
<tr>
<td>$K_v$</td>
<td>Vertical diffusivity coefficient</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>MIMS</td>
<td>Membrane inlet mass spectrometer</td>
</tr>
<tr>
<td>N</td>
<td>Net community production, defined as equation 1.3</td>
</tr>
<tr>
<td>ppm</td>
<td>1 part per million</td>
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<tr>
<td>PS II</td>
<td>Photosystem II</td>
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<tr>
<td>$S_0$</td>
<td>Sea surface salinity</td>
</tr>
<tr>
<td>USW</td>
<td>Underway sea water supply</td>
</tr>
<tr>
<td>VSMOW</td>
<td>Vienna Standard Mean Ocean Water</td>
</tr>
<tr>
<td>$z_{\text{lim}}$</td>
<td>Nutrient limitation index</td>
</tr>
<tr>
<td>$z_{\text{mix}}$</td>
<td>Mixed layer depth</td>
</tr>
<tr>
<td>$z_{\text{NO3}}$</td>
<td>Nitracline</td>
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