Interannual to decadal variability and trends of the oceanic oxygen content in the North Atlantic

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Abstract

This PhD project focuses on the oxygen ($O_2$) variability and trends in the North Atlantic at interannual to decadal time scales. To analyze the decadal trends I performed a careful secondary quality control of the $O_2$ measurements on a new dataset (CARINA) with many previously unpublished hydrographic data in the Atlantic Ocean. The CARINA data were augmented by GLODAP and WOD05 to achieve a good spatial coverage and cover the past five decades. The results from this analysis revealed a significant decrease of $O_2$ concentrations in the Upper (UW), Mode (MW) and Intermediate (IW) Waters with a weighted mean decrease of $-5.1\pm1.7 \mu$mol kg$^{-1}$ over the last 49 years. The observed decrease, however, is not homogeneously distributed, but is largely concentrated in the northeastern and central North Atlantic. Increasing $O_2$ concentrations are observed in the western North Atlantic in the MW and IW. Over the same period the $O_2$ concentrations increased in the Lower Intermediate Water (LIW) and Labrador Sea Water (LSW) throughout the North Atlantic ($5.5\pm2.6 \mu$mol kg$^{-1}$). The observed changes can be attributed to the interplay between circulation and ventilation that affect the $O_2$ concentration in the MW and IW, while changes in solubility seem to be the main driver for the observed decrease in the UW and the increase in the LIW and LSW. Overall, the three upper horizons (UW, MW and IW) have lost $-58\pm20$ Tmol of $O_2$ between 1960 to 2009, and showed an $O_2$ loss to heat gain ratio of $-4.6\pm2.8$ nmol J$^{-1}$. The deeper horizons (LIW and LSW) have gained $70\pm34$ Tmol, showing an $O_2$ to heat ratio of $-2.9\pm1.9$ nmol J$^{-1}$. These ratios are substantially larger than those expected from solubility changes alone, confirming that circulation, ventilation and biology changes tend to enhance the solubility driven changes. For the second analysis, focusing on the interannual to decadal $O_2$ variability, I used 12 hydrographic repeated cruises along the eastern North Atlantic at 47$^\circ$N from 1993 to 2011 with almost yearly resolution until 2005. The analysis focused on the upper 1500 m. The results from this analysis show that the Subpolar Mode Water (SPMW), IW, and Mediterranean Overflow Water (MOW) underwent substantial decadal changes in the $O_2$ concentrations between 1993 and 2002. These changes were associated to circulation, which during this period shows substantial variability due to the northward shift of the Subpolar front (SF) in the eastern North Atlantic. This shift caused more water of subtropical origin to enter into the eastern region, which subsequently reduced the ventilation in the SPMW and therefore lowered the $O_2$ concentration by $-1.8\pm0.7 \mu$mol kg$^{-1}$ yr$^{-1}$. The same circulation changes affected the $O_2$ concentration in the IW, leading to a decrease of $-2.3\pm0.7 \mu$mol kg$^{-1}$ yr$^{-1}$ from 1993 to 2002. I hypothesized that a decrease in the contribution of SAIW along with an increase in the contribution of AAIW and MOW, reduced the $O_2$ concentration in this water mass. The $O_2$ changes in the MOW were affected by a combination of solubility and circulation changes. The attribution of the $O_2$ changes observed after 2002 is difficult, due to the lack of data from 2006 to 2009. Furthermore, interannual changes caused by mesoscale events may be relevant and affect the water column down to at least 1000 m depth. These events could
cause strong changes in the O$_2$ concentration and leading to biases in the estimated variability if not taken into account. The observed long-term O$_2$ trends over the last 50 years (from 1960 to 2009) and the observed variability over the last decades (from 1993 to 2011) in the mode and intermediate waters were associated to the interplay between the North Atlantic Oscillation (NAO) shift that affected the ventilation and circulation of the long-term trends and the wind-stress curl that affected the circulation of the last decades. Further analysis needs to be done to understand the contribution of these two mechanisms to the overall O$_2$ changes in the North Atlantic.
Abstract (Italiano)

Questo progetto di ricerca è incentrato sulla variabilità interannuale e decennale della concentrazione di ossigeno (O₂) nel Nord Atlantico. Per analizzare i trend decennali è stato eseguito un accurato controllo della qualità dei dati sull’O₂ raggruppati all’interno di un nuovo dataset (CARINA). Quest’ultimo raccoglie un numero di dati sull’Oceano Atlantico mai pubblicati in precedenza. Successivamente CARINA è stato integrato con altri dati raccolti in altre due collezioni (GLODAP e WOD05) in modo da aumentare la copertura di dati al livello temporale, includendo gli ultimi 50 anni di osservazioni, e da ricoprire l’intero Nord Atlantico da 35°N a 60°N. I risultati di quest’analisi mostrano un’importante diminuzione della concentrazione di O₂ nelle seguenti masse d’acqua: UW (Upper Water), MW (Mode Water) e IW (Intermediate Water) con una media di −5.1±1.7 μmol kg⁻¹ persi negli ultimi 49 anni. Questa diminuzione non è uniformemente distribuita, ma è largamente concentrata nella parte centrale e nordorientale del Nord Atlantico. La concentrazione di O₂ invece aumenta nel Nord Atlantico occidentale. Nello stesso periodo, l’O₂ aumenta nelle masse d’acqua più profonde (Lower Intermediate Water, LIW e Labrador Sea Water, LSW) in tutto il Nord Atlantico (con una media di 5.5±2.6 μmol kg⁻¹). I cambiamenti della concentrazione di O₂ così osservati sono stati attribuiti ai cambiamenti della circolazione oceanica e della ventilazione delle masse d’acqua, i quali interagiscono nel determinare le concentrazioni di O₂ nelle acque intermedie e modali (UW e MW). La causa principale della diminuzione di O₂ nelle acque superficiali (UW) e dell’aumento di O₂ nelle masse d’acqua più profonde (LIW e LSW) è stata attribuita ai cambiamenti della solubilità dell’acqua. In definitiva, dal 1960 al 2009 le prime tre masse d’acqua (UW, MW e IW) hanno perso O₂ per un ammontare di −58±20 Tmol, con un rapporto tra O₂ perso e calore guadagnato da parte dell’oceano di −4.6±2.8 nmol J⁻¹. Le masse d’acqua più profonde hanno invece guadagnato O₂ per un ammontare di 70±34 Tmol, con un rapporto tra O₂ e calore di −2.9±1.9 nmol J⁻¹. I rapporti tra O₂ e calore calcolati in questa analisi dimostrano che la perdita di O₂ da parte dell’oceano, causata dall’interazione tra circolazione e biologia, è sostanzialmente maggiore rispetto alla perdita che ci si aspetterebbe se si considerasse solo la solubilità. Nella seconda parte del progetto di ricerca, l’analisi è stata concentrata sui cambiamenti interannuali e decennali dell’O₂. Per questo lavoro ho usato dodici campagne idrografiche dal 1993 al 2011, ripetute per più anni consecutivi quasi ogni anno fino al 2005, lungo un transetto nel Nord Atlantico orientale all’altezza di 47°N. Nell’analisi sono stati considerati i primi 1500 metri di profondità. I risultati mostrano che le SPMW (Subpolar Mode Water), IW, e MOW (Mediterranean Overflow Water) sono soggette a una diminuzione di O₂ piuttosto sostanziale tra il 1993 e il 2002. Questi cambiamenti sono stati associati principalmente a cambiamenti nella circolazione oceanica, che durante questo periodo ha subito profonde trasformazioni a causa dello spostamento verso nordovest del fronte polare (SF) situato nel Nord Atlantico orientale. A causa di questo spostamento il contributo nella regione di acque subtropicali è aumentato, di con-
seguenza la ventilazione delle SPMW è diminuita e quindi anche la loro concentrazione di O\textsubscript{2} pari a $-1.8\pm0.7\ \mu\text{mol kg}^{-1}\ \text{yr}^{-1}$. Lo stesso meccanismo produce un effetto simile sulle concentrazioni di O\textsubscript{2} nelle acque intermedie (IW), con una diminuzione pari a $-2.3\pm0.7\ \mu\text{mol kg}^{-1}\ \text{yr}^{-1}$ dal 1993 al 2002. Secondo la mia ipotesi, la diminuzione di O\textsubscript{2} nelle IW è causata dall’aumento dell’apporto di masse d’acqua di origine subtropicale (AAIW e MOW) a discapito di masse d’acqua di origine subpolare (SAIW). Invece, i cambiamenti di O\textsubscript{2} osservati nelle MOW sono probabilmente causati dalla combinazione di due effetti, cioè dai cambiamenti della solubilità e della circolazione. Di difficile determinazione sono invece i cambiamenti osservati dal 2002 al 2011, probabilmente perché tra il 2006 e il 2009 non ci sono osservazioni. Inoltre, cambiamenti interannuali di O\textsubscript{2} possono essere causati anche da eventi a mesoscala il cui effetto può interessare la colonna d’acqua fino a 1000 m di profondità. Questi eventi possono causare enormi cambiamenti nelle concentrazioni di O\textsubscript{2} col rischio che, se non tenuti conto, possono compromettere l’analisi sulla variabilità dell’O\textsubscript{2}. I trend delle concentrazioni di O\textsubscript{2} degli ultimi cinquanta anni (dal 1960 al 2009) e la variabilità decennale (dal 1993 al 2011) osservata nelle acque modali ed intermedie (MW e IW) è stata associata all’interazione tra l’oscillazione Nord Atlantica (NAO) che ha influenzato principalmente la ventilazione e la circolazione delle masse d’acqua degli ultimi cinquanta anni, e del rotore dello sforzo del vento che ha influenzato la circolazione delle masse d’acqua degli ultimi dieci anni. Successive analisi saranno necessarie per stabilire in che modo i due meccanismi interagiscono nel determinare le concentrazioni dell’O\textsubscript{2} nell’oceano.
Chapter 1

Introduction
1. Dissolved Oxygen in the Ocean

Dissolved oxygen is one of the most important constituents in the ocean. Its concentration influences many biological and chemical processes in the ocean, and most of the macroorganisms are physically stressed or die under low oxygen concentration (i.e. when concentrations drop to the level of hypoxia, below 60 to 120 $\mu$mol kg$^{-1}$, or to levels of suboxia below 10 $\mu$mol kg$^{-1}$) (Stramma et al., 2008). Moreover, oceanographers use oxygen also as a tracer for water mass circulation as an indicator for the time when a water parcel was last in contact with the surface ocean. Indeed, once the water parcels escape the euphotic zone, there is no other sources of oxygen and its concentration decreases with increasing age of the subsurface water parcels due to remineralization (Sarmiento and Gruber, 2006; Talley et al., 2011). For these reasons this constituent has been long recognized as a good tracer to detect changes in biological and physical processes. In the following pages all the processes that are involved in determining the concentrations of dissolved oxygen, its distribution and its changes in the ocean will be described.

1.1.1 History and Determination of Oxygen

Oxygen is probably the second most measured chemical oceanographic variable after salinity. Its sampling can be dated back to the end of the 1800s and early 1900 when the first chemical method was proposed by Winkler (1888). This method is still used for the current oxygen measurements with some modification (Carpenter, 1965) with the goal to improve the analytical procedure and its accuracy.

The Winkler titration is an iodometric titration, where iodide ion is reduced into iodine. This reduction is the last step of a multi-step oxygenation. Since the oxygen does not oxidize directly the iodide ion into iodine, a series of reactions is needed, as explained in Hansen (1999). The initial reactions are used to convert the unknown amount of the solute (in this case the dissolved $O_2$ in water) to an equivalent amount of iodine, which may be titrated afterward. The first step is to add a solution of Manganese(II)chloride and alkaline sodium iodide to a sample with a known volume. Manganese precipitates and reacts with the oxygen in the water forming a hydrated tetravalent oxide of manganese (Hansen, 1999).

\[
\begin{align*}
&Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2 \\
&2Mn(OH)_2 + O_2 \rightarrow 2Mn(OH)_3
\end{align*}
\]

The subsequent acidification of the sample dissolves the manganese hydroxide that acts as an oxidizing agent in the acid solution and liberates free iodine from the iodide ions added in the first step with the fixation reagents.

\[
2Mn(OH)_3 + 2I^- + 6H^+ \rightarrow 2Mn^{2+} + I_2 + 6H_2O
\]

The high concentration of sodium iodide solution encourages the formation of triiodide complex

\[
I_2 + I^- \leftrightarrow I_3^-
\]

In the final step, the liberated complex, equivalent to the dissolved oxygen present in the water, is titrated with sodium thiosulphate. The quantity of thiosulphate solution used for the titration gives the
1.1. Dissolved Oxygen in the Ocean

Concentration of oxygen since one mole of oxygen is equivalent to four moles of thiosulphate.

\[ I^-_3 + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} \]  \hspace{1cm} (1.5)

The sodium thiosulphate is not a primary standard and it is subject to deterioration. Therefore any solution of thiosulphate must be standardized with potassium iodide (KIO\(_3\)). The standardization of thiosulphate is conducted by the same procedure and under the same experimental conditions performed for the determination of dissolved oxygen, in order to compensate for possible errors. Other systematic errors may also be introduced before the titration, when the water sample is collected from the Niskin bottles. The most common source of errors is caused by the standardization of the thiosulphate, so only primarily standards of the very best quality must be used. Since there is not an universal primary standard according to Emerson et al. (1999), the secondary KIO\(_3\) standard is dried thoroughly and standardized by the commercially available WAKO standard once or twice a year. This procedure makes it possible to achieve accuracy to slightly less than 0.1% if similar reproducibility is met. Since this kind of procedure is not always used or performed carefully, and since the standards used are not always of the best quality, this is one of the main reasons why many oxygen data collected can not be used. Other sources of error come from the determination of the end-point, that can be visual (using a starch solution as an indicator forming blue complex with iodine molecules) or photometric, with the photometric endpoint considered as the most sensitive method (Carpenter, 1965; Emerson et al., 1999; Williams and Jenkinson, 1982); or from the contamination of the stock solution; or if all the glasswares are not calibrated; or if the titration does not start immediately after acidification of the solution since the iodide solution becomes sensitive to the light; or from the reagent contamination which can be inferred from the reagent blank analysis.

Other methods like the electrochemical sensors (SeaBird CTD) can be used for in situ measurements. This methods is becoming increasingly common as these sensors can provide high resolution and excellent data if they are routinely calibrated against the Winkler titration method (Gilbert et al., 2010). Since oxygen concentrations throughout the ocean and their temporal changes through time are drawing more attention among the oceanographic community for its utility in detecting changes in the ocean circulation and remineralization (see next section), it has been recently proposed to increase the number of O\(_2\) sensors on the ARGO floats that are deployed in the ocean. The ARGO-O\(_2\) sensors can be of two kinds, either an electrochemical sensor whose design is similar to the O\(_2\) sensor on SeaBirds shipboard CTD units Körtzinger et al. (2006) or an optical sensor (the most common is the Aandera Optode). Unfortunately SeaBirds sensor have stability problems over time that cause drifts of up to 15 \(\mu\)mol kg\(^{-1}\) over more than four years (Riser, 2011). Some of the problems can be solved by calibrating the sensor prior deployment in the laboratory and then calibrate the sensor periodically after the deployment by Winkler titration or using archived data. The clear advantage of the ARGO-O\(_2\) floats is the enormous amount of data that can be provide by this sensors, at the moment there are nearly 200 O\(_2\) sensor deployed on ARGO floats (Riser, 2011). If only 20% of the 3000 Argo floats were equipped with these sensors, more than 20000 profiles with 150000 or more measurements in the upper 2000, could be made in one year (Gruber et al., 2007). This will certainly increase the spatial and temporal coverage of the data that at the moment is highly dependent on the shipboard measurements. It would also increase the number of measurements during winter seasons, when the atmospheric conditions make it difficult or impossible to collect bottle data.
1.1.2 Oxygen Distribution

Figure 1.1: Dissolved oxygen distribution along 20° W in the Atlantic Ocean from the WOCE Global Hydrographic Climatology (Gouretski and Koltermann, 2004). Black contours represents the $\sigma_0$ isopycnals, the white line represents the winter mixed layer. The arrows show the circulation pathways (dark red), the ventilation (blue), the gas-exchanges (violet) and the remineralization (green).

Oxygen enters the ocean through air-sea gas exchange, and due to its relatively fast equilibration rate with the atmosphere, its concentration at surface is close to saturation. The air-sea gas flux can be expressed by:

$$\Phi = -k \cdot ([O_2]_a - [O_2]_w)$$  \hspace{1cm} (1.6)

where $\Phi$ is the oxygen flux between the ocean and the atmosphere, $[O_2]_a$ and $[O_2]_w$ are the oxygen concentrations in the air and in the water respectively, $k$ is a parameter that include the gas transfer velocity mainly dependent on the wind speed, and the solubility of the water which is mainly dependent on the temperature. For example, an increase in temperature causes a decrease in the solubility and a subsequent outgassing of oxygen.

The atmosphere however, is not the only source of oxygen for the ocean. Another important source of O$_2$ comes from biology through the photosynthesis/remineralization cycle. In the euphotic zone, autotrophic phytoplankton consume carbon dioxide to produce organic matter and oxygen during photosynthesis. Opposite to the photosynthesis is remineralization, where heterotrophic organisms consume organic carbon and oxygen to produce carbon dioxide. In the euphotic zone, organic matter production exceeds respiration, resulting in the net production of oxygen. In the deeper layers the remineralization rate increases, exceeding photosynthesis and causing a net consumption of oxygen.
1.1. Dissolved Oxygen in the Ocean

Once a water parcel is no longer in contact with the surface ocean it carries a surface water $O_2$ signature defined as preformed oxygen (Sarmiento and Gruber, 2006), at depth due to remineralization process the oxygen concentrations change, thus the observed oxygen is the sum of these two components. Since at the surface the ocean oxygen is close to the saturation concentration, we can use this information to assume that the $[O_2]_{preformed} = [O_2]_{sat}$. With this assumption we can quantify the change in $O_2$ due to remineralization by calculating the Apparent Oxygen Utilization (AOU) with this formula:

$$AOU = [O_2]_{sat} - [O_2]_{observed}$$ (1.7)

where $[O_2]_{sat}$ and $[O_2]_{observed}$ are the saturated and the measured oxygen concentrations in the ocean respectively. We can use the oxygen saturation variable in place of $[O_2]_{preformed}$ since at the surface ocean the oxygen is generally close to the equilibration because of the fast exchange at the air-sea interface. However, $[O_2]_{preformed}$ and $[O_2]_{sat}$ do not always correspond exactly, and the actual preformed oxygen is not exactly at saturation (Sarmiento and Gruber, 2006). The oxygen does not always fully equilibrate with the atmosphere in response to heating/cooling of the surface, and this can occur particularly in the high-latitudes during winter time (Ito et al., 2004).

These two mechanisms, the gas-exchange and the photosynthesis/remineralization effect explain why the concentration of oxygen is high at surface and it decreases at depth. If these where the only two mechanisms involved in the distribution of the oxygen in the ocean, the oxygen would continue to decrease until the bottom, but this is not the case as one can easily see from Fig. 1.1. What we observe in this figure is that after a minimum concentration at mid-depth usually not deeper than 1000 m depth, the oxygen starts to increase again. The reason is that in the ocean the water mass circulation plays a critical role in distributing properties horizontally and vertically. More in detail, we can actually distinguish between the ‘pure’ circulation effect which role is distributing water properties along its path, and the exchange between the highly oxygenated water in the mixed layer and the lower oxygenated water at deeper layers, the latter called ventilation. These two mechanisms are difficult to distinguish and often they are considered as just one mechanism referred to as a circulation effect, while the ventilation is considered only a mechanism that occurs in the surface ocean as a consequence of change in the air-sea $O_2$ disequilibrium. Once the deeper water masses are ventilated they move forward along circulation pathway where the oxygen is then consumed by remineralization along his path and the residual can reach the deep ocean.

If we observe several vertical oxygen profiles along the Pacific and Atlantic Ocean (Fig. 1.2), we can observe how its distribution is influenced by all these mechanisms. For example, the oxygen rich water that penetrates into the deep North Atlantic as North Atlantic Deep Water (NADW), can be easily identified along the western margin of South America far away from his formation place (red profile in Fig. 1.2). We can also identify the Labrador Sea Water (LSW) in the Labrador Sea as a huge volume of nearly homogeneous water with high oxygen content (yellow profile in Fig. 1.2). It is also possible to identify the horizontal oxygen minimum zone (OMZ) in the tropical Pacific (violet profile in Fig. 1.2). Extended horizontal oxygen minimum zones (OMZs) exist in the eastern tropical gyres (the largest in the Pacific). Also the Indian Ocean (in the Arabian Sea) has the largest volume of suboxic water. These zones are a consequence of a combination of sluggish ocean ventilation, enhanced respiration (e.g. Stramma et al. (2008); Karstensen et al. (2008)), and low initial oxygen (Gruber, 2004). Highly distinguishable in the figure is also the circulation and remineralization effects, in which the profiles...
reach their minimum. Another important thing to highlight is the difference between the Pacific Ocean and the Atlantic Ocean. From the profiles it is clear that the Atlantic Ocean has on average higher concentration of oxygen compared to the Pacific, especially in the deeper ocean. This is an indication that the Atlantic Ocean is characterized by younger water masses that are newly ventilated and have higher oxygen concentrations, while the Pacific Ocean is characterized by older water masses that have been away from the surface for a longer time (Talley et al., 2011).

1.1.3 Drivers of Changes in Oxygen Concentration

The changes in oxygen concentration in the ocean therefore reflect changes of one or more of these mechanisms. This makes oxygen one of the most useful tracers of ocean biogeochemistry. We can summarize this in the following equation:

\[
\frac{dO_2}{dt} = \frac{dO_2}{dt}_{\text{bio}} + \frac{dO_2}{dt}_{\text{circ}} + \frac{dO_2}{dt}_{\text{vent}} + \frac{dO_2}{dt}_{\text{heat}} + \frac{dO_2}{dt}_{\text{diseq}}
\] (1.8)

Changes in O₂ concentrations can be caused by changes in the organic matter export, and/or by changes of the fraction of the export flux that is oxidized at a given depth, all these summarized by the term \(\frac{dO_2}{dt}_{\text{bio}}\); the term \(\frac{dO_2}{dt}_{\text{circ}}\) refers to the changes in the O₂ due to changes in the rate at which newly O₂-rich waters are circulated through the interior or changes in the circulation pathway, while the \(\frac{dO_2}{dt}_{\text{vent}}\) refers to the changes in the transfer of this O₂-rich waters across the mixed layer (Deutsch et al., 2006). The \(\frac{dO_2}{dt}_{\text{heat}}\) represents the changes in solubility due to changes in the heat content of the water, and finally the \(\frac{dO_2}{dt}_{\text{diseq}}\) represents the changes in the air-sea O₂ disequilibrium of surface waters when a water parcel loses contact with the atmosphere.

The remineralization and circulation are tightly connected, indeed the separation of the two mechanisms is quite problematic. An increase in stratification increases the residence time of water in the
substrate ocean, allowing for more organic matter remineralization to occur within a given water mass, and so reduces oxygen concentrations in the ocean interior (Matear and Hirst, 2003). On the other hand an increase in stratification could reduce the export production as part of an overall decline associated with a reduced supply of nutrients to the upper ocean, causing an increase of O_2 concentrations (Matear and Hirst, 2003). The tendency for subsurface O_2 to decline under increased stratification is predicted by most of the models, indeed stratification leads to strengthening the organic pathway (i.e. the transport of nutrients into subsurface water as sinking particulate organic matter) compared to the inorganic pathway (i.e. downward mixing of the nutrients in their inorganic form), causing a net lowering of the O_2 concentration in the subsurface waters due to remineralization increase (Keeling et al., 2010). Because it is difficult to separate the biological term from the circulation and ventilation, we can combine the three terms together and the equation becomes simplified as follow:

\[
\frac{dO_2}{dt} = \frac{dO_2}{dt} |_{bio,transp} + \frac{dO_2}{dt} |_{heat} = \frac{d(-AOU)}{dt} + \frac{dO_{2,sat}}{dt}
\]  (1.9)

with the term \( trsp \) in \( \frac{dO_2}{dt} |_{bio,transp} \) including both circulation and ventilation.

The separation of AOU into circulation, remineralization and ventilation processes can be done for example by using oceanographic tracers to detect the rates of ocean transport and mixing. In this way we could compute the time rate of change of AOU with this formula:

\[
OUR = \frac{dAOU}{dt}
\]  (1.10)

where OUR represents the Oxygen Utilization Rate associated with the remineralization of organic matter. The OUR can be calculated by knowing the time required for a water parcel on a given potential density surface to transit from a high-latitude region where water of that density outcrops at the surface (Keeling et al., 2010), this rate is generally called ventilation age. It is important at this point to notice that the term ventilation can be considered on different perspectives. Some have used the terms ventilation to refer to all processes that supply atmospheric oxygen into the ocean interior, including the gas-exchanges between the ocean and atmosphere interface, the exchange between the surface mixed layer and the subsurface layers and the circulation in the ocean interior (for example Keeling et al. (2010)), others like Deutsch et al. (2006) used the term ventilation in a more specific way, referring to ventilation only to the combination of air-sea exchange at the surface and the exchange between the mixed layer. Here, ventilation is referred to the only exchange between the mixed layer and the subsurface waters and separate from the gas exchange effect at the surface ocean. So the terms ventilation ages used in Keeling et al. (2010) and Sarmiento and Gruber (2006) refers to the wider definition which includes the circulation effect. The estimation of this rate can be done from the distribution of radiocarbon, tritium or chlorofluorocarbons (CFCs) in the ocean. Also knowing the decrease in the sinking flux of organic matter with depth can help estimate OUR (Keeling et al., 2010; Martin et al., 1987), but unfortunately accurate estimate of OUR is still not completely and satisfactory resolved despite its importance.

The changes in the ocean ventilation can be inferred by using the potential vorticity. Potential vorticity is a dynamical property of a fluid, analogous to angular momentum. Conservation of potential vorticity is one of the most important concepts in geophysical fluid dynamics (Talley et al., 2011). Potential vorticity is conserved whenever there are no forces (other than gravity) on the fluid and no buoyancy
Chapter 1. Introduction

sources that can change density. This means that a water parcel conserves the value of potential vorticity that it obtains wherever a force acts on it, and when it leaves the ocean surface it keeps the same value of potential vorticity after they enter the ocean interior where forces like friction are much weaker (Talley et al., 2011), unless the water parcel upwells again or enters the western boundary currents (Hanawa and Talley, 2001). Low potential vorticities are a signature of recent outcropping due to deep water convection while high potential vorticities are signature of water well protected from ventilation (Johnson and Gruber, 2007). Johnson and Gruber (2007) demonstrated a strong correlation between changes in AOU and potential vorticity, where an increase in potential vorticity was followed by increase in the AOU (decrease in $O_2$) due to decrease in the ventilation.

Another separation can be achieved between the gas-exchange component of the oxygen concentration and all the other components that are not affected by the air-sea flux. This separation can be done by analyzing the trend in the quasi-conservative tracer, $O^*_2 = O_2 - r_{O_2:PO_4}PO_4$, where $r_{O_2:PO_4}$ is the oxygen to phosphorus ratio of biological uptake/release. $O^*_2$ is a tracer that reflects the $O_2$ gained or lost by a water parcel through air-sea gas exchange, irrespective of whether this exchange occurs as a result of biological consumption and production of $O_2$ in the surface ocean or whether it is the result of heating and cooling the surface (Gruber et al., 2001; Keeling and Garcia, 2002). This second separation thus consists of the following:

$$\frac{dO_2}{dt} = \frac{dO_2}{dt}|_{gasex} + \frac{dO_2}{dt}|_{no-gasex} = \frac{dO^*_2}{dt} + \frac{(r_{O_2:PO_4}PO_4)}{dt}$$

(1.11)

where the no-gasex component includes all processes at the surface and interior that did not leave an imprint on the air-sea exchange. This could be biology, transport and mixing, and heat fluxes. $O^*_2$ can be considered a qualitatively tracer for ventilation. Indeed, variation in the ocean ventilation controls which fraction of the biologically produced oxygen is transported into the ocean’s interior. A weak ventilation would cause a reduction of the $O^*_2$ since would cause a larger loss of the biologically produced oxygen to the atmosphere. A strong ocean ventilation would tend to cause a larger gain of this biological oxygen to the ocean’s interior and thus causing an increase in the $O^*_2$. However, since other processes such as heating and cooling of the surface ocean control the $O^*_2$, the interpretation of this parameter can be only qualitatively.

1.1.4 Long-term Oxygen Changes

The alteration of oxygen concentrations in a changing ocean is becoming of a great interest, and several studies have examined changes in the oxygen in different ocean basin. Fig. 1.3 from Keeling et al. (2010) shows a summary of all the works that have found changing oxygen concentrations (mostly decrease) in the water column.

Studies by Emerson et al. (2001); Watanabe et al. (2001); Ono et al. (2001); Keller et al. (2002); Emerson et al. (2004); Whitney et al. (2007), for the Pacific Ocean, Garcia et al. (1998); Johnson and Gruber (2007); Stramma et al. (2008) for the Atlantic Ocean, and Bindoff and McDougall (2000) for the Indian Ocean, describe decrease in oxygen mainly in the upper thermocline of the ocean. In the Indian Ocean McDonagh et al. (2005) shows instead an increase in dissolved oxygen from 1987 to 2002. More in detail, for the North Pacific, Emerson et al. (2004) present an increase in AOU from
1.1. Dissolved Oxygen in the Ocean


Figure 1.3: Summary of all the works that have shown changes in the oxygen concentration in the ocean (from Keeling et al. (2010)). The authors label the studies using the first letter of first author’s last name and a two-digit year. For details see the Table 3 in Keeling et al. (2010).

the mid 1980s to the mid 1990s with a maximum change centered near the density horizon $\sigma_\theta = 26.6$. Ono et al. (2001); Watanabe et al. (2001) describe increases in AOU from 1968 to present between $\sigma_\theta 26.7–27.2$ and from 1980s to 1990s between $\sigma_\theta 26.4–27.4$ respectively. Whitney et al. (2007) observed a decrease in oxygen from 1956 to 2006 at the Ocean Station Papa from below the ocean mixed layer to a depth of at least 1000 m. In the Indian Ocean, Bindoff and McDougall (2000) found a decrease in the upper thermocline oxygen concentration comparing data with a median date 1962 with a hydrographic section in 1987. For the Pacific Ocean, changes in the ventilation rate of the water masses that outcrop locally in the individual basins have been suggested by Emerson et al. (2004); Watanabe et al. (2001); Ono et al. (2001); Deutsch et al. (2005), and decadal variations in circulation have been suggested by Deutsch et al. (2005). The results from Whitney et al. (2007) also shows a bidecadal variability where two periods of virtually no ventilation with decrease in $O_2$ concentrations in the late 1960 and 1990s are followed by periods of oxygen enrichment that may be associated with increased tidal mixing amongst the Kuril and Aleutian Islands. The tidal mixing helps to break down the surface halocline so that the stratification decrease, thereby promoting convection and ventilation (Yasuda et al., 2006; Whitney et al., 2007). Whitney et al. (2007) also show that the hypoxic boundary has shoaled from 400 to 300 m and that hypoxia may increase in the subarctic Pacific due to global warming as upper ocean stratification increases. As we learned oxygen concentrations can drop also to suboxic level, and the eastern equatorial Pacific is one of the biggest areas where the intermediate
waters are suboxic forming this oxygen minimum zone. Stramma et al. (2008) shows that during the last 50 years there was a vertical expansion of the OMZ. For the Indian Ocean, Bindoff and McDougall (2000) explains the decrease in oxygen by a slight slowing of the subtropical gyre allowing more time for biological consumption to decrease the oxygen concentration by water parcel translation from the formation area to the observation point.

Garcia et al. (1998) identified a decrease in the O$_2$ concentration between 1981 and 1992 in the subtropical North Atlantic, with the largest changes occurring between 700 m and 1700 m. The maximum O$_2$ decrease at 1100m depth coincided with the maximum potential temperature and salinity increase. They found a broad zonal uniformity of the average temperature, salinity, and O$_2$ changes across the basin near 1100 m that suggested natural changes in the source water characteristics entering 24.5°N. They explained the O$_2$ decrease by measurement error (30%) and the change in solubility (20%) due to warming. Garcia et al. (1998) tried also to compute the rate of decrease of O$_2$ consumption (decrease in OUR) and compare it with the nutrient concentrations to find a corresponding regenerative increase of nutrient. Indeed, during the in situ degradation of organic matter, O$_2$ is consumed and nutrients are released in constant stoichiometric ratios (Redfield ratio), If the changes in oxygen consumption are due to in situ consumption of O$_2$ as a result of organic degradation, the nitrate and phosphate should reflect corresponding changes. But they found small changes in the nutrients over the same time period, indicating that biological remineralization was not the major cause of the decreasing O$_2$ concentration. Johnson and Gruber (2007) investigated the decadal water mass variations in the north-eastern Atlantic Ocean along the transect at 20°W (between 20°N and Iceland) from 1988 to 2003 and found large increases of AOU at the base of the Subpolar Mode Water (SPMW). They hypothesized that changes in wind-driven ocean circulation and air-sea heat flux associated with the shift toward lower positive value of the NAO (North Atlantic Oscillation) index, are responsible for the increase in AOU and potential vorticity observed at the base of SPMW. Indeed it has been observed that the shift from high positive index to low positive or negative index causes a northwestward shift of the North Atlantic Current (NAC), since the SPMW that originates on the southeastern side of the NAC ventilates at lighter density than the SPMW that originates on the northwestern side of the NAC. A shift of the NAC towards the northwest would bring lighter, saltier and warmer water with high AOU and potential vorticity at lighter density horizons northwestward. Low AOU and low potential vorticity are signatures of recent outcropping due to deep water convection while high AOU and potential vorticity are signatures of water well protected from ventilation and far removed from their source regions (as for example the waters in the permanent pycnocline) (Johnson and Gruber, 2007). In their study Johnson and Gruber (2007) found a large increase in AOU and potential vorticity at the base of SPMW that suggested a decrease in the deep convection. Even though they emphasized NAO-associated variability, Johnson and Gruber (2007) did not exclude the hypothesis that a long-term warming trend in the ocean could also result in ventilation of lighter and shallower winter mixed layers with time that could cause the observed changes in AOU and potential vorticity. Stramma et al. (2008) focus on the OMZs and show that the OMZ in the tropical Atlantic Ocean has vertically expanded during the last 50 years. In particular, the Atlantic Ocean time series show that the decline in oxygen content has been most intense in the tropical Atlantic.

To summarize from all these works it seems that the main driven of the O$_2$ changes are primarily physical, resulting from changes in ocean circulation and ventilation rather than biological. Moreover, aside
from a few studies where for small regions it was possible to have a time series of more than 30 years (Whitney et al., 2007; Stramma et al., 2008), all the other works were based on fewer observations often derived from the analysis of repeated transect which observation occurred not every year and which temporal coverage is not longer than 20 years, making difficult to draw firm conclusions about global trends (Keeling et al., 2010). According to Gilbert et al. (2010) comparing the summary results from published time series over the 1976-200 period with the results from time series calculated from raw data over the same period, there is a significant difference between published and calculated trends for the open ocean, suggesting that there is a possible tendency to more frequently publish papers with negative oxygen trends in open ocean rather than no trends or positive trends. Furthermore according to Gilbert et al. (2010), given that the ocean is often affected by interannual, decadal and centennial variability, the comparison of repeated transect which data are collected several years apart could lead to erroneous conclusions in regards to the $O_2$ trends. Moreover Gilbert et al. (2010) show through a probability density function that for shorter time periods there is a tendency to see oxygen trends of greater amplitude (positive or negative).

### 1.2 North Atlantic Ocean

In this thesis, the North Atlantic Ocean is defined as the area of the Atlantic between 65° and 30° North. The North Atlantic is characterized by a sea floor topography that strongly impacts the circulation of the water masses. According to Sy et al. (1997) and Kieke et al. (2009) the see-floor topography can indeed constrain deep circulation, and even the upper ocean circulation as well (Bower et al., 2002). The main topographic features are shown in Fig.1.4. From this figure we can see the Mid-Atlantic

![North Atlantic topography derived from the TerrainBase gridded at 5-minute intervals.](image-url)
Ridge, as a long underwater mountain chain, cuts the North Atlantic into two main basins, the North American Basin and the West European Basin. The Mid-Atlantic Ridge extends until Iceland where it actually emerges at the surface on the island. The northern part of the ridge, however, is called Reykjanes Ridge and is partly separated from the Mid Atlantic Ridge by some fracture zones with the deepest one called Charlie Gibbs Fracture Zone. The Charlie Gibbs Fracture Zone represents an important connection between the deep west and east basins allowing an inter-basin exchange of surface and deep water masses (Kieke, 2005). Furthermore, the northern part of the North Atlantic, usually the domain of the subpolar gyre, is shallower than the southern part. In the northern part the topography forms some small basins and seas, the Iceland basin in between the Reykjanes Ridge and the Rockall Plateau, the Irminger Sea between the Reykjanes Ridge and Greenland, and the Labrador Sea between Greenland and Canada. Between Iceland and England we also see the Iceland Scotland Ridge, and this is also an important place of exchange between water of subpolar origin and water of arctic origin. Also relevant are: the Rockall Trough between the Rockall Plateau and Ireland which is another exchange passage between the North Atlantic and the Nordic Seas, the Porcupine Bank that divides the subpolar and subtropical gyres (Lozier and Stewart, 2008), and the Strait of Gibraltar between the Iberian Peninsula and North Africa that connects the Atlantic Ocean to the saltier and warmer Mediterranean Sea.

I focus my study on the North Atlantic for several reasons, the most practical one is that the North Atlantic is among all the other ocean basin the one with the best data coverage in terms of both spatial and temporal distribution. Despite the availability of a huge amount of data, as stated above, few studies focused on long-term oxygen trends and on time scales longer than 20-30 years. These studies have shown already a potential decrease in the oxygen concentration that is worth further investigation in light of the fact that these changes might be attributed to global warming. This brings us to the other reason, the North Atlantic is subject to substantial interannual to decadal changes in connection with the North Atlantic Oscillation (NAO) (Visbeck et al., 2003), permitting the investigation of oxygen variability in connection with this climate pattern.

As I explained in the previous section, circulation affects the distribution of oxygen in the ocean, and this is immediately evident from Fig 1.1 if we observe the oxygen distribution versus the isopycnals contour lines. Moreover, most of the analysis that will be presented in subsequent chapters is done on isopycnal layers with the goal to identify the oxygen changes in the main water masses. It is therefore important to briefly explain the North Atlantic surface and deep circulation in the next section. Moreover, because the NAO is the main mode of interannual atmospheric variability in the North Atlantic I will review this climate pattern in the following section.

### 1.2.1 North Atlantic Circulation

**Surface Circulation**

Fig. 1.5 shows the surface circulation in the North Atlantic which includes a cyclonic gyre (subpolar gyre) and an anticyclonic gyre (subtropical gyre), this chematic is based on Talley et al. (2011). The subtropical gyre has a strong western boundary current composed by the Gulf Stream System and the North Atlantic Current System, and an eastern boundary upwelling system represented by the Portugal...
Figure 1.5: North Atlantic surface circulation schematics based on Talley et al. (2011).

Current System and the Canary Current system (not shown in the figure) (Talley et al., 2011). The Gulf Stream carries eastward in the North Atlantic a surface core of warm and saline water (Bower et al., 2002; Bower and Von Appen, 2008; Talley et al., 2011). The North Atlantic Current (NAC) from the Grand Bank of Newfoundland flows eastward and separates into several branches (Bower et al., 2002; Bower and Von Appen, 2008). The southernmost branch becomes part of the subtropical gyre while the northern part feeds the subpolar gyre (Talley et al., 2011).

The subpolar gyre also has its western boundary currents, the Eastern Greenland Current (EGC) and the Labrador Current that are connected by an eastern boundary current called Western Greenland current (WEG). The southern side of the Subpolar gyre is represented by the NAC that flows eastward and separates into several branches that flow northeastward toward the Nordic Seas, with the northern branch representing the Subpolar Front (SF) (Bower and Von Appen, 2008). From the figure it is also possible to see how the NAC connects the subpolar and the subtropical gyre.

With increasing depth, the subtropical gyre shrinks westward and northward toward the Gulf Stream System, and gyre circulation can be seen as a multiple layers of streamlines that subduct into the interior ocean. The gyre is directed ventilated where streamlines are connected to the sea surface, while the deeper layers, that are not directly connected with the surface, are not ventilated (Talley et al., 2011).

The subpolar gyre with increasing depth becomes closed south of the Greenland-Faroe ridge, its surface current structure extend to the ocean bottom although it is diminished in strength at depth. In the subpolar gyre there are no regions of subduction and the ventilation is due to buoyancy-driven circulation through convection or brine rejection (Talley et al., 2011).
Intermediate and Deep Circulation

Fig. 1.6 shows the schematic intermediate and deep circulation in the North Atlantic based on Talley et al. (2011) for the upper circulation, Kieke (2005) for the Labrador Sea Water (LSW) and deeper water circulation, and Lozier and Stewart (2008) for the circulation of the Mediterranean Overflow Water (MOW). Part of the upper circulation is included in the figure as well (in red and orange) since Subpolar Mode Water (SPMW) forms from the NAC. I will explain in detail the main water masses of the North Atlantic in the next subsection.

![Figure 1.6: North Atlantic intermediate and deep circulation schematics based on Talley et al. (2011); Kieke (2005); Lozier and Stewart (2008). In red and orange the upper ocean circulation (important for the formation of the SPMW as depicted by Talley et al. (2011)). In brown the Mediterranean Overflow Water (MOW) as depicted by Lozier and Stewart (2008). In pink the Labrador Sea Water (LSW) as depicted by Kieke (2005), with the convection regions (pink circles). In Blue are the Deep Western Boundary currents and the Iceland Scotland Overflow Water (ISOW). Finally in black is the Antarctic Bottom Water (AABW).](image)

The deep circulation from 2500-4000 dbar (in blue) is characterized by cold and dense water that flows northward along western margins of the Iceland, Irminger, Labrador and Newfoundland Basins. These waters are named Deep Western Boundary Current (DWBCs) and are fed by the cold and dense water from the Denmark Strait and from the Iceland Scotland Overflow Water (ISOW) that originate in the Nordic Seas (Kieke, 2005). DWBCs are found along the western boundary of the Atlantic that can be associated with the North Atlantic Deep Water (NADW) and with the Antarctic Bottom Water (AABW).

The intermediate circulation from 500-2000 dbar (pink and brown), is mainly characterized by the circulation of LSW from its place of formation in the Labrador Sea and occasionally in the Irminger Sea and from the spreading of the MOW that originates in the Mediterranean Sea and has a distin-
guishable high salinity content (Lozier and Stewart, 2008). Both these water masses will be discussed in the following subsection together with the SPMW (not show in the figure) and the STMW and Subartic Intermediate Water.

Water Masses in the North Atlantic

The deep circulation is often described in terms of water masses, since the direction of the flow is often inferred from property distributions (Talley et al., 2011). With these criteria it is possible to distinguish between several water masses in the North Atlantic that will be considered later in the analysis of the oxygen changes. Since the focus of this thesis is on the upper 2000 m, I will describe only the water masses that lie above these depths.

Mode waters. SPMWs are surface water masses with nearly uniform properties in the vertical as well as in the horizontal (Hanawa and Talley, 2001), confined between the ocean surface and the permanent pycnocline. They have densities of $\sigma_\theta = 26.9 - 27.75 \text{ kg m}^{-3}$. This is the most significant mode water in the subpolar region due to its volume and impact on internal ocean properties (Talley et al., 2011). It is generally more than 400 m thick. Mode water formation is usually associated with wintertime convective mixing due to bouyancy loss from the ocean surface and the formation areas occur on the low density side of permanent fronts (Hanawa and Talley, 2001). The warmest and lightest SPMW (26.9 $\sigma_\theta$ and 14°C) is found east and south the NAC. As the NAC moves eastward, its SPMW becomes progressively colder and denser. While the lightest part of the SPMW subducts southward into the subtropical gyre, the densest part does not subduct but instead continues in the surface layer becoming progressively colder, fresher and denser toward the north following the several branches of the NAC. Each of these branches has its SPMW in its eastern warm side. (Brambilla and Talley, 2008). This surface layer is obviously affected by the air-sea fluxes that cause a diapycnal flux that primarily transforms SPMW from lower to higher densities. It is not correct to imagine the transformation of an entire SPMW directly into the next denser SPMW, which is the simplified hypothesis of McCartney and Talley (1982). The fist hypothesis by McCartney and Talley (1982), was that the SPWMs formed during the late winter convection follow the cyclonic circulation of the subpolar gyre, gradually increasing their density. The final products of this water mass transformation are the Labrador Sea Water (LSW) and the dense water masses formed in the Nordic Seas. These water masses participate substantially in the upper flow of the overturning circulation. The new hypothesis from Brambilla and Talley (2008) confirms that SPMWs are part of the surface layer, extending vertically from the ocean surface to the permanent pycnocline, but that the SPMW are associated with several northeastward currents and that they are not connected by cyclonic flow. SPMW can be identified by a minimum of isopycnal potential vorticity that corresponds to high vertical homogeneity of the water mass.

The North Atlantic Subtropical Mode Waters (STMW) are water masses found between the seasonal and permanent thermocline in the northwestern and central portion of the subtropical gyre in the western North Atlantic ocean south the Gulf Stream (Peng et al., 2006). The temperature is about 18°C, for this reason it is also called Eighteen Degree Water (EDW) and it can be seen on any vertical section crossing the Gulf Stream (Talley et al., 2011). It has relatively homogeneous properties centered at about 18°C, a salinity of 36.5 and a $\sigma_\theta$ equal to 26.5 kg m$^{-3}$ (Hanawa and Talley, 2001). The STMW
layer has been observed to ventilate to depths as great as 900 m, with a mean penetration of about 287 m and a mean thickness of about 200 m (Peng et al., 2006). New water is produced at the end of each winter through convection driven by intense wintertime buoyancy loss (McCartney and Talley, 1982). The winter vertical convection takes place in the so-called subduction zone (New et al., 1995) where sloping isopycnals outcrop at the surface in the Sargasso Sea.

**Intermediate waters.** Below the surface layer and pycnocline, at intermediate depths of about 500–1500 m, the Intermediate Water (IW) in the North Atlantic are represented by the SAIW (Subarctic Intermediate Water) and the Mediterranean Overflow Water (MOW) and Antarctic Intermediate Water (AAIW). VanAken and de Boer (1995) defined the IW in the eastern subpolar North Atlantic as a layer with low-oxygen waters of southern origin, these waters represent a mixture of the Mediterranean Overflow Water (MOW) advected northward along the European slope into the Rockall Trough (Reid, 1979), the AAIW brought to the region by the NAC (Tsuchiya et al., 1992; Alvarez et al., 2004) and water of subpolar origin, with the uncertain contribution of each of these water masses to the overall IW layer (Sarafanov et al., 2008). Sometimes the SAIW is simply denoted as IW or Arctic Intermediate Water (AIW). To avoid further confusion I will use the generic term IW as defined by Sarafanov et al. (2008) as the layer marked by oxygen minimum and relatively low salinity to distinguish it from the MOW that, despite being marked by oxygen minimum, it also has high salinity concentrations. In a $\theta$–S–O$_2$ diagram the IW would be defined as the water masses with low salinity concentrations centered at the oxygen minimum range. The IW subducts beneath the NAC (Arhan, 1990; Pollard et al., 2004) and is carried by the NAC into the Iceland Basin north and west of the Southern Branch of the NAC (Pollard et al., 2004).

The MOW enters the Atlantic Ocean from the Strait of Gibraltar and flows northward, reaching its neutral buoyancy and depth of 1000-1500 m by about Cape St. Vincent (Candela, 2001). After exiting the strait, these waters mix with the surrounding waters in the Gulf of Cadiz (Baringer and Price, 1997), and flow as a coherent mid-depth boundary current along the eastern coast of the North Atlantic. This boundary currents continues along the Iberian Peninsula, into the Bay of Biscay and onward toward the Porcupine Bank (Lozier and Stewart, 2008). The MOW pathway is sketched in Fig. 1.6 and includes the pathway (dashed arrows) in the northeastern basin that is climatically variable (Lozier and Stewart, 2008).

**Labrador Sea Water.** LSW is the intermediate water mass that spreads within the North Atlantic subpolar gyre and further propagates southward in the Deep Western Boundary Current forming the lower limb of the Meridional Overturning circulation. LSW is characterized by a salinity minimum in the subpolar North Atlantic, a minimum in potential vorticity in the subpolar North Atlantic and subtropical western boundary region and a maximum in oxygen and CFCs (Talley et al., 2011). Water masses formed by wintertime convection in the northern North Atlantic are rich in oxygen due to their recent contact with the atmosphere. The LSW forms in the Labrador Sea and occasionally in the Irminger Sea as well (Kieke et al., 2006) as the final product of SPMW that enters the Labrador Sea from the Irminger Sea. From Fig. 1.6 it is possible to see the pathway of the LSW after is formation.
1.2. North Atlantic Ocean

1.2.2 North Atlantic Oscillation

The North Atlantic Oscillation (NAO) is the dominant mode of atmospheric variability in the North Atlantic (Visbeck et al., 2003). It refers to a redistribution of atmospheric mass between the Arctic and the subtropical Atlantic. A shift from one phase to another produce large changes in the mean wind speed and direction over the North Atlantic, the movement of moisture and heat from the Atlantic to the continents, and in the path and intensification of storms (Hurrell et al., 2003). In the so called positive phase, the climatological meridional atmospheric pressure gradient is enhanced due to higher-than-normal surface pressures south of 55°N in combination with a broad region of anomalously low pressure throughout the Arctic. The large pressure difference causes the westerlies to shift northward relative to their mean position (Talley et al., 2011). The largest amplitude anomalies occur in the vicinity of Iceland and across the Iberian Peninsula. In fact, the traditional NAO index is the difference in pressure between Portugal and Iceland (Fig. 1.7), although other indices are also used.

Regarding the ocean response to the changes in the NAO index, during periods of high positive NAO state, the winter ocean heat loss is intensified together with the intensification and expansion of the subpolar gyre. This creates a negative temperature anomaly in the subpolar gyre in the area southeast of Greenland, and west of North Africa, and a positive temperature anomaly over the North American Basin (Visbeck et al., 2003) (Fig. 1.8). During low positive and negative NAO phases, weakening of the convection happens coupled with an increase in the northward advection of subtropical water that causes an increase in temperature and salinity in the subpolar gyre southeast of Greenland and west of North Africa with an opposite negative temperature anomaly in the North American Basin (Visbeck et al., 2003) (Fig. 1.8) and a reduction of the extension of the subpolar gyre. During the last 50 years the NAO index evolved from a strong negative phase in the late 1960 to the early 1970s to a low positive and low negative phases during the late 1970s until late 1980s. Then NAO changed to a

Figure 1.7: North Atlantic Oscillation index (December-March) represented by the blue for negative and red for positive index. Black line is a filtered index computed by using a backward-looking position of a 17-point Blackman filter and then advanced by 1 year to simulate the effects of the ocean circulation memory and lagged response to the NAO as used by Johnson and Gruber (2007).
prolonged high positive phase in 1990s until 1995. After this strong positive phase the index started to decrease to lower positive and sometime negative phases in mid 1990s until now.

The shape of the subpolar gyre is strongly affected by the NAO oscillation and hence its circulation (Bersch, 2002). During a persistently positive high NAO period, the subpolar gyre cyclonic circulation intensifies and expands and it is accompanied by intense convection. The subpolar front (SF) shifts westward in the Newfoundland Basin and the southward transport along the slope of Grand Banks is reduced while the eastward transport of cold and fresh water from the Labrador Sea is enhanced (Bersch et al., 2007). On the other side of the MAR, in the Western European Basin, the SF shifts southeastward, blocking the way to subtropical water to advect in the subpolar gyre reducing the amount of warm and saline water in the northern regions (Bersch et al., 2007; Häkkinen and Rhines, 2009; Burkholder and Lozier, 2011). This results in a decrease in temperature and salinity in the intermediate-deep water column in the northern North Atlantic (Häkkinen and Rhines, 2004, 2009; Bersch, 2002; Bersch et al., 2007; Sarafanov, 2009), as schematically sketched in the left panel of Fig. 1.8. Moreover, the eastward shift of the SF limits the northward advection of MOW and thus produces negative salinity anomalies in the Rockall Trough at the MOW levels (Lozier and Stewart, 2008; Burkholder and Lozier, 2011; Bozec et al., 2011). Conversely, during low NAO period (weak forcing), the SF moves southeastward in the Newfoundland Basin increasing the southward transport of subpolar water thorough the Labrador Current. East of the MAR, in the Western European Basin, the SF shifts westward coupled with weak deep convection and increases northward advection of subtropical waters and MOW, resulting in positive salinity anomalies in the Rockall Trough.

A recent study from Häkkinen et al. (2011) shows, however, that the strength of the subpolar and subtropical gyres seems to be modulated by the wind-stress curl pattern, which forms the gyres in the

Figure 1.8: Ocean response to the NAO oscillation. The ellipses represent the direct responses to positive or negative NAO. With positive (negative) NAO a negative (positive) temperature anomaly represented with the blue (red) ellipses is created in the subpolar gyre (SPG) south of Greenland and west of North Africa, and a positive (negative) temperature anomaly represented with red (blue) ellipses over North American Basin. Prolonged positive NAO states causes changes in the gyre circulation represented in the figures with the arrows. Yellow arrows represent the SPG circulation, the eastern side is the northernmost NAC branch which represents the Subpolar Front (SF). The other two branches are represented in light orange and dark orange (southernmost branch). Dash red arrow sketches the subtropical gyre (STG) circulation, and the reddish-purple arrows represent the MOW northward pathway. Larger (smaller) pink circles indicates stronger (weaker) deep convection. Black arrows indicate the direction of the movements of the SF.
first place. According to their empirical orthogonal function (EOF) analysis of the wind-stress curl, the first EOF mode, which fluctuates closely with the NAO index, does not give the most important mode as a leading mode of the strength of the gyres. It is the second EOF mode that has a larger impact than the first mode on the gyres strength, and this mode, although has many features in common with the NAO, appears to be separated from the NAO variability.

### 1.3 Goals and Outline

The goal of this work is to improve our knowledge on the dissolved oxygen changes in the North Atlantic water masses over the last decades. There are few studies that had investigated the changes of this parameter for more than 20 years and for wide areas. The first part of my project focused on answering this particular question, i.e., to be able to reconstruct the oxygen trend in the main water masses in the North Atlantic of the last five decades. Moreover we have learned that although the mechanisms driving these changes are well known, the contribution of each mechanism to the total change is still not well constrained. This problem will be addressed in the second part of the project where I will examine the interannual changes and the driving mechanisms responsible for these changes in the eastern North Atlantic.

For the first part of the project, I used three different datasets for the North Atlantic, GLODAP (GLObal Ocean Data Analysis Project), CARINA (Carbon IN the Atlantic) and selected data from the World Ocean Database 2005 (WOD5), merged together to have a large dataset that allowed me to investigate the last 50 years of oxygen trends. This exercise was more than a simple merger of the three datasets, but the key point was instead to have an internally consistent high quality dataset. This is of fundamental importance, since errors in the data can lead to erroneous conclusions and the detection of changes that are not real. Chapter 2 will be presented the work done to perform the secondary quality control on the oxygen measurements on the CARINA dataset. This work was part of an international collaborative effort of the European project CARBOOCEAN, and United States partners. Information about this synthesis project can be found on this webpage [http://cdiac.ornl.gov/oceans/CARINA/about_carina.html](http://cdiac.ornl.gov/oceans/CARINA/about_carina.html). This work was published on *Earth System Science Data (ESSD)* journal, thus the chapter will be structured as the published version.

In chapter 3 results from the 50 years trend analysis will be presented and discussed. The chapter will be structured as a paper with an introduction, method, results, discussion and conclusions sections. In chapter 4 I will present the results from the interannual to decadal variability of the oxygen concentration analysis, also structured in the same way as chapter 3. Finally summary and outlook will be presented in the final chapter of this dissertation.
Chapter 2

CARINA oxygen data in the Atlantic Ocean

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Abstract

In the CARINA (Carbon dioxide in the Atlantic Ocean) project, a new dataset with many previously unpublished hydrographic data from the Atlantic, Arctic and Southern Ocean was assembled and subjected to careful quality control (QC) procedures. Here, we present the dissolved oxygen measurements in the Atlantic region of the dataset and describe in detail the secondary QC procedures that aim to ensure that the data are internally consistent. This is achieved by a cross-over analysis, i.e. the comparison of deep ocean data at places that were sampled by different cruises at different times. Initial adjustments to the individual cruises were then determined by an inverse procedure that computes a set of adjustments that requires the minimum amount of adjustment and at the same time reduces the offsets in an optimal manner. The initial adjustments were then reviewed by the CARINA members, and only those that passed the following two criteria were adopted: (i) the region is not subject to substantial temporal variability, and (ii) the adjustment must be based on at least three stations from each cruise. No adjustment was recommended for cruises that did not fit these criteria. The final CARINA-Oxygen dataset has 103414 oxygen samples from 9491 stations obtained during 98 cruises covering three decades. The sampling density of the oxygen data is particularly good in the North Atlantic north of about 40°N especially after 1987. In contrast, the sample density in the South Atlantic is much lower. Some cruises appear to have poor data quality, and were subsequently omitted from the adjusted dataset. Of the data included in the adjusted dataset, 20% were adjusted with a mean adjustment of 2%. Due to the achieved internal consistency, the resulting product is well suited to produce an improved climatology or to study long-term changes in the oxygen content of the ocean. However, the adjusted dataset is not necessarily better suited than the unadjusted data to address questions that require a high level of accuracy, such as the computation of the saturation state.
Data coverage and parameters measured

Repository-Reference: doi:10.3334/CDIAC/otg.CARINA.ATL.V1.0
http://cdiac.ornl.gov/ftp/oceans/CARINA/CARINA_Database/CARINA.ATL.V1.0/
Available at: http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html
Coverage: 60°S–75°N; 80°W–34°E
Location Name: Atlantic Ocean
Date/Time Start: 1977-10-07
Date/Time End: 2006-02-02

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For a complete list of parameters see Key et al. (2010).
2.1 Introduction

CARINA (Carbon dioxide in the Atlantic Ocean) is a data synthesis project with the aim to assemble a large collection of ocean interior data from hydrographic cruises in the Arctic, Atlantic and Southern Ocean, many of which were previously unavailable to the public (Tanhua et al., 2010a). Because the CARINA dataset consists of data collected by many different laboratories over several decades and often using different methods, these data need to be carefully quality controlled in order to obtain datasets that are useful for describing the large-scale distribution of properties. In addition, if the goal is to study long-term trends, it is crucial to obtain an internally consistent dataset, which can only be achieved by applying secondary quality control (QC) procedures to the data (Key et al., 2004; Lamb et al., 2002; Johnson et al., 2001).

While the primary QC consists in the identification of the outliers and errors in the data, the secondary QC consists of the quantification and reduction of the analytical errors in the reported values without the elimination of real temporal changes (Johnson et al., 2001). The goal is to ensure internal consistency. Given the lack of traceable standards for many oceanographic variables, including oxygen and nutrients, the secondary QC may not result in more accurate values, however. For the purpose of the analysis of long-term changes, internal consistency is sufficient. However, if the goal is to compute the magnitude and variability of the air-sea gas exchange of oxygen, then high accuracy is required and this product may not provide it. The quality of the data and the offsets are assessed using a crossover analysis whereby property differences between individual cruises on deep-ocean isopycnals...
2.2. Data

are quantified. Such a crossover analysis is based on the assumption that the investigated properties, e.g. oxygen, salinity and nutrients, in the deep waters have not changed in between the individual cruises (Lamb et al., 2002), so that the identified difference is usually attributed to an analytical error. On the basis of the identified offsets, a set of adjustments is inferred that is then applied to the original data in order to obtain an adjusted, internally consistent data set (see e.g. the GLobal Ocean Data Analysis Project (GLODAP) (Key et al., 2004)).

As part of the CARINA project in the Atlantic Ocean, the primary and secondary QC has been undertaken for the following parameters: salinity (Tanhua et al., 2010a), total inorganic carbon (TCO$_2$) (Pierrot et al., 2010), total alkalinity (TA) (Velo et al., 2009), nitrate, phosphate, silicic acid (Tanhua et al., 2009), oxygen (this study), CFC-11, CFC-12, CFC-13 and CCl$_4$ (Steinfeldt et al., 2010). Details can be found in Key et al. (2010) and Tanhua et al. (2010b) in this issue, as they describe the methods developed for the primary and secondary QC and the assemblage of the dataset.

The aim of this paper is to describe the oxygen data in the CARINA dataset, to document the quality control procedures applied to the oxygen data, and to justify all the adjustments.

2.2 Data

CARINA consists of a collection of 188 hydrographic cruises or projects, divided into three regions, the Atlantic (CARINA-ATL), the Arctic Mediterranean Seas (CARINA-AMS) and the Southern Ocean (CARINA-SO) regions. This paper focuses on the oxygen data from the Atlantic Ocean, which is the region with the highest number of cruises (98 cruises). The CARINA-ATL region has five cruises in common with the CARINA-AMS group and five cruises in common with the CARINA-SO group, in order to ensure consistency across the three regions.

For the secondary quality control, six hydrographic cruises from the World Ocean Circulation Experiment (WOCE) as synthesized by GLODAP (Key et al., 2004) were added to ensure consistency with this prior synthesis effort. The GLODAP project performed a rigorous secondary quality control on the carbon data, however regarding the oxygen adjustments, GLODAP group applied the biases de-
Chapter 2. CARINA oxygen data in the Atlantic Ocean
determined by Gouretski and Jancke (2000) in their analysis of the WOCE and historical hydrographic data. The data from these reference cruises are not included in the final product. Twenty-nine cruises from the CARINA-ATL dataset were identified as core cruises, primarily on the basis of their having a good spatial distribution and a higher expected data quality. During the computation of the adjustments, more weight was given to these core cruises as well as to the six WOCE cruises, ensuring that cruises with lower data quality are not causing unwarranted adjustments in the cruises with higher data quality.

2.2.1 Oxygen data

![Maps showing the temporal distribution (5 year intervals) of stations that have oxygen samples in the final product of CARINA-ATL (without the 6 reference cruises from GLODAP, see Sect. 2): (a) 1977 to 1981; (b) 1982 to 1986; (c) 1987 to 1991; (d) 1992 to 1996; (e) 1997 to 2001, and (f) 2002 to 2007.](image)

The CARINA-ATL dataset contains 103414 oxygen samples from 9491 stations. A map of the locations of the hydrographic stations with at least one oxygen sample (Fig. 2.1) shows that CARINA-ATL has a good spatial distribution, with the densest coverage in the northeast Atlantic. The data span three decades, with the earliest samples stemming from 1977 and the latest samples taken in 2006 (Fig. 2.2). The majority of the data stem from the 1990s, with a reasonably good coverage between 1990 and 2005. The years 1997, 1998, 2001 and 2003 have the greatest number of samples, largely driven by the fact that these years include basin-wide transects (Fig. 2.3). Maps of the data from 1977 to 2007 with a time step of five years show that from 1992 to 2007 the spatial coverage is good, and particularly in the last five years is dominated by long transects (Fig. 2.3). From 1987 to 1991 the data
are especially concentrated in the northeastern part, while from 1977 to 1986 there are only few data stemming from along the Iberian coast. The only cruise in 1977 (29CS19771007 cruise # 51) is one of the Galicia cruises (Galicia4) and has 88 stations with oxygen data only in the upper 1500 m. For this reason, we did not include this cruise in the secondary QC, i.e. no adjustment is recommended (Table 2.1). For similar reasons, eight other cruises were not considered in the second QC and labeled as NC (Not Considered) in Table 2.1.

In order to provide an overview of the oxygen distribution, we plot in Fig. 2.4 the oxygen data versus depth for 11 large-scale regions, separating the time periods by color. This plot reveals, for example, that all oxygen data before 1986 are from the upper 2000 m only (green dots in panel d). The vertical distribution of oxygen in the Atlantic Ocean reflects the combined effects of gas exchange, the photosynthesis/remineralization cycle, and ocean circulation. Near the surface ocean, rapid gas exchange keeps oxygen very near the saturation concentration (Sarmiento and Gruber, 2006), despite oxygen production from photosynthesis and oxygen demand by the upwelling/mixing of low oxygen waters from below. In the interior, the oxygen demand from the remineralization of the sinking organic matter leads to decreasing oxygen concentrations, but this decrease is modified strongly by the level by which ocean circulation and mixing are able to transport oxygen from the upper ocean into the deep. For example, oxygen rich water penetrates into the deep North Atlantic as a result of the southward spreading of recently ventilated North Atlantic Deep Water. This easily identifiable water mass that occupies the depths between 1000 m to 4000 m and extends southward from the Labrador Sea to the Antarctic Divergence (Fig. 2.4, panel c, e, and g). The Labrador Sea Water (LSW) is also distinguishable in the Labrador Sea as a huge volume of nearly homogeneous water with high oxygen content. This water mass is a product of winter deep convection (Fig. 2.4 northwest region, panel a). In the intermediate-depth eastern tropical ocean (Fig. 2.4 the eastern region in the tropical zones, panel f) it is also possible to identify the horizontal oxygen minimum zone (OMZ).
Chapter 2. CARINA oxygen data in the Atlantic Ocean

![Diagram showing CARINA oxygen data in the Atlantic Ocean](image-url)
2.3 Methods

All CARINA data were first subjected to a primary QC, i.e. the detection and flagging of outliers and other irregular data points (Tanhua et al., 2010b). Our subgroup was responsible for the secondary QC of the oxygen data. The method used for the secondary QC is described in detail by Tanhua et al. (2010b). We briefly summarize here this method with emphasis on the issues specific to oxygen.

The first step of the secondary QC consists of a crossover analysis (e.g. Johnson et al., 2001), where the difference is computed between two cruises (defined as an offset) that are crossing each other or, as is often the case in the Atlantic, are along repeated tracks. For the computations of the offsets, only data deeper than 1500 dbar (about 1500 m) were used in order to eliminate from the analysis the upper water column that is more variable in time. The quality control procedures/criteria differed for two cruises, cruise # 93 and # 107. These cruises were added in the later stage of the project, and because they have only few samples deeper than 1500 m, the minimum depth for the crossovers was set manually at 1000 m. For each crossover, stations were selected from an area that was within a radius of 2 degrees of latitude (i.e. about 222 km). In order to better compare samples in the deep ocean, the analysis was performed on \( \sigma_4 \) density surfaces. For each oxygen sample, its corresponding density was first computed, and then the data from each profile were interpolated with a Piecewise Cubic Hermite interpolating scheme to a number of standard densities. Those were selected in such a way that the interpolated values were equally distributed in depth space (Tanhua et al., 2010b). The oxygen offsets and their standard deviations were computed as multiplicative factors. We opted for a multiplicative instead of an additive approach for two primary reasons: First, this avoids the potential problem of obtaining negative values in low oxygen regions. Second, this reflects the fact that the preparation of the standard is the most likely source of error for the measurement, and this source of error is of multiplicative nature (see also Tanhua et al., 2010b). We suspect that choosing an additive approach would not have resulted in a drastically different adjusted dataset since the range of oxygen values in the North Atlantic is relatively limited, so that there is little expected difference between a multiplicative and additive approach.

To perform the crossover analysis we used the running cluster routine developed by Tanhua et al. (2010a). In this routine, the offset is computed by first comparing each station from the first cruise to each station from the second cruise in the crossing area, and then by computing the weighted mean and standard deviation of the differences. Relative to other crossover analysis methods, this running cluster
method minimizes the potential for comparing stations that sample different hydrographic settings and also minimizes the need for a manual definition of subregions.

The second step of the secondary QC consists of the computation of an optimal set of adjustments that are then applied to the data in order to generate an internally consistent data set. This is achieved by writing the problem as a system of linear equations that relate the data in each cruise to those in all crossing cruises and then inverting this matrix to find a set of adjustments that minimizes the offsets among all the cruises (Johnson et al., 2001). Three variants of a least square method were used: the (unweighted) Simple Least Squares (SLSQ) method, the Weighted Least Square (WLSQ) method, and the Weighted Damped Least Square (WDLSQ) method (Johnson et al., 2001; Tanhua et al., 2010a). For the WLSQ schemes, the inverse of the standard deviation of the offsets were used as weights. In addition, for the WDLSQ schemes, the reference and core cruises were weighted higher than the other cruises in order to ensure a lower level of adjustments in these cruises compared to the others. Finally, the weights included also a temporal term, in order to give less weight to offsets that are between cruises that sampled a region many years apart. This is achieved by multiplying the standard deviation of the crossovers with a time factor $K_T$ computed as follows:

$$K_T = 1 + 0.1 \Delta_{\text{year}}$$

where, $\Delta_{\text{year}}$ represents the time in years between the two cruises.

We use the results from the WDLSQ variant for further processing, but we show that the other variants give similar results. As the offsets for oxygen were computed as multiplicative factors, the adjustments were of a multiplicative nature as well.

The third step of the secondary QC consists of the careful cruise-by-cruise inspection and evaluation of the suggested adjustments. This step was undertaken manually by the CARINA analysts. It was decided that only cruises for which adjustments larger than 1% difference from 1, i.e. smaller than 0.99 or larger than 1.01 were considered. If in doubt, for example, if there were indications that an apparent offset was driven by true variability, no adjustment is proposed. A detailed discussion for those cruises that required special attention is provided below. The cruises with an adjustment of less than 1% from 1 are not adjusted, i.e. an adjustment factor of 1 is proposed instead.

As a last step, the overall level of internal consistency of the CARINA-ATL oxygen data was computed using the weighted mean (WM) of the absolute values of the offset ($D$) of $L$ crossovers with their uncertainty ($\sigma$). (Note that Tanhua et al. (2009) refers to this quantity as the overall “accuracy” of the dataset).

$$WM = \frac{\sum_{i=1}^{L} D(i)/\sigma(i)^2}{\sum_{i=1}^{L} 1/\sigma(i)^2}$$

This analysis gives a level of internal consistency of 0.8% (Fig. 2.5). For a typical ocean interior oxygen concentration of 250 $\mu$mol kg$^{-1}$, this translates into a level of consistency of 2 $\mu$mol kg$^{-1}$, i.e. the estimated level of consistency is about a factor of two larger than the typical precision of dissolved oxygen measurements.
2.4 Results

The offset analysis computed by the automated cluster routine reveals a large range of multiplicative offsets for oxygen, from more than 0.9 to less than 1.1 (Fig. 2.6a). However, given the substantial uncertainty in the offsets, 43% of the crossovers are statistically indistinguishable from 1. The smallest offset of 0.89 with a standard deviation of 0.01 exists between the Discovery cruise 74DI19890511 (cruise # 165) and the Meteor cruise 06MT19960910 (cruise # 15). This offset is driven mainly by the first cruise for which an upward adjustment of 1.11 will be proposed (see subsection 4.1.3).

Regarding the second cruise (see Table 2.1), we also propose an adjustment of 0.985. The biggest offset of 1.11 with a standard deviation of 0.01 corresponds to the offset between the C. Darwin cruise 74AB19910501 (cruise # 160) and the Discovery cruise in 1989 (74DI19890511). The offset is driven by the Discovery cruise, while the C. Darwin cruise (see Table 2.1) does not need an adjustment.

After the first round of the inversion, the remaining offsets are much smaller, largely independent of which inversion method is used (Fig. 2.6b–d). In the case of the SLSQ the offset reduction leads to 77% of all cruise offsets being indistinguishable from 1, while for WLSQ and WDLSQ, this percentage is 73%. The suggested offsets for each cruise computed by the WDLSQ method (shown in black in Fig. 2.7) generally cluster in between our threshold barriers (0.99 to 1.01), but there are a significant number of cruises that require much larger adjustments. Particularly noteworthy are the following cruises: 74DI19890511 (cruise # 165) with the biggest upward adjustment of 1.11; cruises 74DI19890612 (cruise # 166) and 74DI19890716 (cruise # 167) that require adjustments of 1.07, cruises 74AB19910712 (cruise # 162) and 74AB19900528 (cruise # 159) needing adjustments of 1.06, cruise 29GD19821110 (cruise # 53) that needs an upward adjustment of 1.04, and finally cruise 64TR19900701 (cruise # 155) that needs an adjustment of 1.02 and cruises 64TR19900714 (cruise # 156), and 64TR1990408 (cruise # 157) for which an adjustment of 1.015 is proposed. Regarding the downward adjustments, noteworthy are the cruises 06MT19970107 (cruise # 16) that according to the WDLSQ inversion needs an adjustment of 0.94, and cruise 06MT19920509 (cruise # 9) that requires a downward adjustment of 0.96. Also relevant are cruises 18HU19941012(cruise # 42), 06MT19960613

Figure 2.5: Plot of the offsets calculated for each crossover in the final product of CARINA-ATL after adjustments have been applied. WL: the weighted mean of the offsets; F: the percentage of offsets indistinguishable from 1 within their uncertainty; L: the number of crossovers.
Figure 2.6: Plot of the offsets for each crossover (red dots) and their uncertainties (black error bars). The offsets from the reference cruises are also included in the figure. The first row, i.e. (a–d) corresponds to the results before any suggested adjustment have been applied, while the second row, i.e. (e–h) corresponds to the results after the manually edited adjustments were applied. First column, i.e. (a) and (e), show the results from the offset analysis ordered by offset. The second, third, and forth columns depict the offsets after the inversions. (b) and (f) are results from the Simple least Square method (SLSQ), (c) and (g) are results from Weighted Least Square method (WLSQ), and (d) and (h) are results from the Weighted Damped Least Square method (WDLSQ). The red numbers in the upper-left corner of each panel are the percentage of crossovers that are statistically indistinguishable from zero.

(cruise # 14), 18HU19931105 (cruise # 40), 33RO19980123 (cruise # 85), 06MT19990610 (cruise # 20) and 74DI19970807 (cruise # 171) that according to the WDLSQ inversion need adjustments of 0.98. Cruise 74DI19970807 is a special case that will be discussed in Subsect. 4.1.9.

The manual editing process used these results and evaluated for each cruise whether the suggested adjustment was warranted or not. In general, no adjustment was applied if the suggested adjustment was within the 1% threshold barriers, while the adjustment suggested by WDLSQ was adopted in the other cases. Special cases are discussed below.

The distribution of the offsets after the manually edited adjustments have been applied is shown in Fig. 2.6e. The adjustments substantially reduced the number of crossovers that are statistically different from 1, i.e. from 57% to 35%, but it did not reduce it down to zero. This is due to two factors: First, the 1% threshold was used even in cases where the recommended adjustment was significantly different from zero; second, some cruises were not adjusted despite them having substantial offsets.

To check the results we re-ran the three inversions (Fig. 2.6f–h) and re-computed the adjustments
2.5 Discussion of special cases

In this section we discuss the cruises that during our evaluation needed special consideration. We provide here only the summary statements. More details, such as figures from each crossover as well as more detailed comments about each cruise can be found at http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html. The cruises are identified with an expocode that contains the country information, ship information, and the date of when the ship left the port.

**cruise 74AB19900528 cruise # 159**

This cruise took place in the eastern part of the Mid-Atlantic Ridge from 28 May to 15 June 1990, covering a small area with 71 stations. Only 3 stations have oxygen data and only 1 station has samples from depths greater than 500 m. Although the inversion suggested a substantial adjustment of 1.06 (see Table 2.1), this result is insufficient to warrant action as it is based on a single station. We agreed to label the cruise as NC (no suggestion of adjustment possible) in the on-line table and to flag this cruise for oxygen because of the uncertainty about the quality of the data.
cruise 29CS19930510 cruise # 52

This cruise took place from 10 May to 1 June 1993, covering 92 stations located off the western coast of Iberian Peninsula. The WDLSQ inversion suggested a downward adjustment of 0.982 (see Fig. 2.7). Because of the coastal location of the cruise with less than an half of the stations deeper than 1500 m, and because the crossovers did not reveal clear offsets, especially those with the core cruises, we recommend no adjustment for this cruise.

cruise 74DI19890511 cruise # 165

This cruise (from 11 May to 7 June 1989) has 990 stations along a section from 46°N to 60°N on 20°W; along another section from 23°W and 59°N to 8°W and 56°N, and a station group centered on 23°W and 59°N. Almost all data are from the top 250 m. Only 5 stations have oxygen data deeper than 1500 m, and for those stations the inversion gave an adjustment of 1.11. This is outside the range in order for these data to be considered to be good enough to be included in the dataset. For that reason we agreed to flag the entire cruise for oxygen because of the poor quality of the data.

cruise 74DI19890612 cruise # 166

This cruise (from 12 June to 9 July 1989) took place in the area 46°–60°N and 10°–22°W and has 87 stations, but only 3 stations have deep oxygen data. As was the case with the previous Discovery cruise (74DI19890511), we agreed to flag the oxygen data as questionable from the entire cruise because of the lack of sufficient deep data and too high offsets.

cruise 74DI19890716 cruise # 167

This cruise (from 16 June to 10 August 1989) has 34 stations with 17 of them containing deep oxygen data that can be compared with other cruises in the same area. Also for this Discovery cruise the inversion suggested a substantial upward adjustment, i.e. 1.07 (Table 2.1). The vertical O$_2$ profiles reveal a lot of scatter in the data. Taking into account the large suggested adjustment and in order to be consistent with the decisions regarding the previous Discovery cruises (see Subsects. 4.1.3 and 4.1.4), we decided to flag the oxygen data as questionable.

cruise 29GD19840218 cruise # 55

This cruise (18 February to 7 March 1984) is one of the Galicia cruises (Galicia 7) that took place off the northwestern part of the Iberian Peninsula. It has 33 stations but none of them have oxygen data from deeper than about 2000 m. Although the inversion WDLSQ suggested a downward adjustment of about 0.98 (see Table 2.1 and Fig. 2.7), we agreed that no adjustment was warranted. The main arguments were (i) the lack of deep oxygen data, and (ii) the lack of clear offsets to other cruises.
2.5. Discussion of special cases

Cruises 06MT19920316, 06MT19920509 and 06MT19920701 cruises # 8, 9 and 10

Originally those three cruises were considered as a single cruise 06MT19920322. But differing offsets (especially those for salinity) made it clear that this cruise needs to split into three single cruises. For oxygen, only the 06MT19920509 has stations with enough oxygen data to compute the offsets to the other cruise of the dataset, while cruises 06MT19920316 and 06MT19920701 do not have oxygen measurements. The cruise 06MT19920509, as shown by the solution from the inversion WDLSQ (Fig. 2.7), needs a conspicuous upward adjustment of 0.96 that we applied at the final product.

cruise 74AB20050501 cruise # 164

This cruise is an Atlantic zonal section at 36°N. With 144 full depth stations. The inversion suggests a downward adjustment of 0.99. However, the crossovers with core cruises reveals that the oxygen data from this cruise are higher only in the western part of the transect, while no offsets are evident in the eastern part. We checked the cruise report and we saw that the first 43 stations had a calibration problem. Based on this evidence we agreed to split the cruise into two parts: stations 1 to 43, for which we recommend an adjustment of 0.94 in agreement with the crossover offsets with the two core cruises 316N19970815 and 316N20031013; and a second part from stations 44 to 144, which does not require an adjustment as evidenced by its high consistency with the core cruise 33RO20030604.

cruise 74DI19970807 cruise # 171

This core cruise took place from 7 August to 17 September 1997 and has 143 stations along four different sections: a long section from 60°N and 43°W (south coast of Greenland) to 40°N and 9°W (western coast of Iberian Peninsula), a section from 63°N and 20°W (south of Iceland) to 57°N and 8°W crossing the Iceland Basin and the Rockall Plateau, a short section of 9 stations from 63°N and 41°W to 61.4°N and 35.7°W in the Irminger Sea, and a group of 8 stations in the northern part of the Irminger Sea at around 65°N from 27 to 30°W. The WDLSQ inversion suggests an adjustment of 0.98, but this is not confirmed by the crossovers with other core cruises. Moreover, considering that this cruise has 4 different sections, and that one of them is located just south of the Iceland where the ocean exhibits high temporal variability, we recommend no adjustment for this cruise.

This cruise as well as # 12 and # 13 (see subsection 4.1.10) was included in the GLODAP dataset despite the fact that we generally exclude cruises that were in GLODAP (Tanhua et al., 2010a). These cruises were added to CARINA because additional parameters, critical to the CARINA goals, became available after GLODAP was published (Tanhua et al., 2009). In GLODAP (cruise # 25 in GLODAP), a correction of -6.79 µmol kg⁻¹ was applied to this particular cruise based on Gouretski and Jancke (2000) (note that the corrections are of additive kind). This corresponds to an about 2% downward adjustment, in line with what our inversion suggested. Since our analysis included a careful cruise-by-cruise inspection and evaluation of the suggested adjustments including a full documentation of the results (http://cdiac.ornl.gov/ftp/oceans/CARINA/CARINA_Database/CARINA. ATL.V1.0/), while in GLODAP the oxygen corrections were taken straight from a previous work based on Gouretski and Jancke (2000), we recommend to use the data from the CARINA dataset for
Chapter 2. CARINA oxygen data in the Atlantic Ocean

this cruise.

cruises 06MT19941012 and 06MT19941115 cruises # 12, and 13

These cruises are also present in the GLODAP database, and were included in CARINA for the same reasons as cruise # 171. GLODAP has applied slightly different adjustments, -3.01 µmol kg$^{-1}$ for cruise # 12 and -0.17 µmol kg$^{-1}$ for cruise # 13. These adjustments are small and lower than our threshold (1%) above which we made adjustments. Indeed, the offsets between these unadjusted CARINA cruises and their corresponding adjusted GLODAP representation are negligible.

2.6 Summary and Conclusions

Based on the secondary quality control of the CARINA-Oxygen dataset, we recommend adjustments for 23 out of the 98 cruises. Most adjustments were between ±1% and ±2% with only five cruises needing an adjustment larger than 2%. In addition, we regard the data from 4 cruises as of insufficient quality for climate-type studies, and therefore recommend these data to be flagged. However, this affects only 2002 data points out of the 103414 oxygen samples in the CARINA-Oxygen dataset. We also suggest an adjustment for a reference cruise (317519930704) that will not appear in the final product. This is consistent with the adjustment proposed by Johnson and Gruber (2007) but different from GLODAP where two different adjustments were inadvertently applied at the same time (Table 10 note d Sabine et al., 2005).

The quality controlled oxygen data in the CARINA-Oxygen data will constitute a rich source of information to explore the impact of climate variability and change on the ocean’s oxygen cycle and to extend the analysis conducted thus far in the Atlantic (e.g. Johnson et al., 2005; Johnson and Gruber, 2007). Oxygen is one of the best tracers to detect changes in biological and physical processes in the ocean’s interior (Plattner et al., 2002; Deutsch et al., 2005; Körtzinger et al., 2006) because of its high signal-to-noise ratio. Its signal is particularly large because the physical and biological processes driving oxygen variability tend to enhance each other (Gruber et al., 2001). This is different from dissolved inorganic carbon, for which most processes tend to lead to opposing effects (Gruber and Sarmiento, 2002). As a result, one expects substantial decreases in the ocean’s oxygen content in the future, since ocean warming and increased stratification will reduce the ocean’s holding capacity for oxygen and the replenishment of the interior ocean with oxygen from the near surface (Matear et al., 2000; Plattner et al., 2002; Bopp et al., 2002; Keeling et al., 2010). This may be exacerbated by ocean acidification, which will lead to reduced production of mineral CaCO$_3$ and hence less ballasting, causing the exported organic matter to remineralize at shallower depth. As a consequence, the thermocline regions with already low oxygen may substantially expand (Oschlies et al., 2008; Hoffmann and Schellnhuber, 2009; Keeling et al., 2010). Such expansions of the oxygen minimum zones have been observed (Stramma et al., 2008), although it is presently unclear whether this is already a consequence of climate change.

The sparsity of the hydrographic observations of O$_2$ makes estimates of inventory changes difficult (Hamme and Keeling, 2008), so the data that have been collected must be utilized to the fullest and
centralized. Much insight has been already gained by the analysis of historical O$_2$ data measured during the latter decades of the 20th century revealing large-scale changes in subsurface O$_2$ concentration in different basins of the global ocean (Johnson and Gruber, 2007; Emerson et al., 2001; Bindoff and McDougall, 2000). Thus we expect the CARINA dataset, with excellent temporal and spatial coverage as well as careful quality control, will serve as a critical resource for the research community. Furthermore, combining the CARINA oxygen data with the quality controlled carbon data from the CARINA-carbon dataset (Pierrot et al., 2010) along with other tracers (Steinfeldt et al., 2010; Tanhua et al., 2010a, 2009; Velo et al., 2009), provides us with a unique opportunity toward describing the recent changes in ocean biogeochemistry.
Table 2.1: Table of adjustments estimated from WDLSQ method. The column # indicates the cruise number in the final product. The columns “Core” and “Ref” identify the core and references cruises (marked as x). The inversion method adjustment column refers to the results from the WDLSQ inversion with the corresponding mean and standard deviation in the subcolums. The recommendation column represents the adjustment proposed on the base of the crossover analysis and inversions, the cruises in common with the two other groups are labeled as ATL+AMS and ATL+SO. The reference cruises are included in the table and marked with stars in the # column although they will not be included in the final CARINA product. The cruises where it was not possible to compute the adjustment are labeled as NC (not considered), the cruises where it was not possible to suggest an adjustment because of few or no data are labeled as ND. The cruises that belong the CARINA-AMS group are label as AMS. The last two columns are the references for the oxygen samples and the chief scientists of the cruises.

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- **a** The original cruise 06MT19920322 was several legs, so we split the cruise into three: 06MT19920316, 06MT19920509 and 06MT19920701.
- **b** NC because only one crossover for this cruise.
- **c** No deep data so not included in the 2nd level QC.
- **d** Recommended by the AMS group.
- **e** Added in the later stage of the project, because few samples deeper than 1500 m, the minimum depth for the crossovers was set manually at 1000 m.
- **f** No deep data for the stations in the North Atlantic. Recommended by the AMS group.
- **g** The first number refers to the adjustment recommended only from stations 1 to 43, the second number refers to no adjustment from station 44 to last.

## Acknowledgements

This work was supported by funds from ETH Zurich. We are grateful to T. Tanhua for his valuable contribution and for leading the ATL group. We thank the numerous scientists and analysts responsible for the collection, and the analysis of the large amount of data that form the CARINA dataset. Without their contribution this project would not have been possible.
Chapter 3

Oxygen trends over five decades in the North Atlantic

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Abstract

We investigate long-term trends in dissolved oxygen in the North Atlantic from 1960 to 2009 on the basis of a newly assembled high-quality dataset consisting of oxygen data from three different sources CARINA, GLODAP and the World Ocean Database. Oxygen trends were determined along isopycnal surfaces for eight regions using a least-squares linear regression method. Our results show a significant decrease of oxygen in the Upper (UW), Mode (MW) and Intermediate (IW) waters in almost all regions over the last 5 decades. Over the same period, oxygen increased in the Lower Intermediate Water (LIW) and Labrador Sea Water (LSW) throughout the North Atlantic. The observed oxygen decreases in the MW and IW of the northern and eastern regions are largely driven by changes in circulation and/or ventilation, while changes in solubility are the main driver for the oxygen decrease in the UW and the increases in the LIW and LSW. From 1960 until 2009 the UW, MW, and IW horizons have lost a total of $-58\pm20$ Tmol, while the LIW and LSW horizons have gained $70\pm34$ Tmol. We find only limited evidence of an impact of anthropogenic climate change. Comparing our oxygen trends with those of the oceanic heat content, we find an $O_2$ loss to heat gain ratio of $-4.6\pm2.8$ nmol J$^{-1}$ for the UW, MW and IW, and a ratio of $-2.9\pm1.6$ nmol J$^{-1}$ for the LIW and LSW. These ratios are substantially larger than those expected from solubility alone.
3.1 Introduction

Dissolved oxygen tends to respond very sensitively to climate variability and change because a particular perturbation in sea-surface temperature not only changes the solubility of dissolved oxygen, but also alters upper ocean stratification in a way that tends to amplify the solubility effect (Najjar and Keeling, 2000; Gruber et al., 2001; Keeling and Garcia, 2002; Plattner et al., 2002; Bopp et al., 2002; Keeling et al., 2010). This amplification is a result of ocean stratification affecting the supply of oxygen from the near-surface ocean, where oxygen is produced by photosynthesis or reset by air-sea exchange, into the ocean’s interior, where it is consumed by heterotrophic respiration (Sarmiento and Gruber, 2006). This high sensitivity to climate forcing makes oxygen one of the best candidates for detecting and better understanding the link between global warming and the resulting biogeochemical and physical changes in the ocean (Joos et al., 2003; Deutsch et al., 2005; Körtzinger et al., 2006; Brennan et al., 2008; Keeling et al., 2010, e.g.). The amplification also implies that the ocean likely will lose a substantial amount of oxygen in the coming decades and centuries in response to global warming, a process termed “ocean deoxygenation” (Keeling et al., 2010). Global models suggest a loss of between 1 to 7% for this century for a business as usual scenario (Matear and Hirst, 2003; Frölicher et al., 2009) with an oxygen loss to heat gain ratio of about $-5 \text{ nmol O}_2 \text{ J}^{-1}$.

Several studies reported long-term decreases in the oxygen content in the interior ocean (Bindoff and McDougall, 2000; Emerson et al., 2001; Johnson and Gruber, 2007; Whitney et al., 2007; Stramma et al., 2008, 2010, e.g.) (see summary in Keeling et al. (2010)) consistent with the expectation of a warming ocean losing oxygen. However, the vast majority of studies reported trends over 20 years or less, and only a few looked at trends over 40 years and more (Watanabe et al., 2003; Whitney et al., 2007; Stramma et al., 2008). Great caution needs to be used when interpreting trends over 20 years or less in the context of global warming (Gruber, 2009). Interannual-to-decadal variations are substantial, and will influence the determination of long-term trends, particularly when considering that most of these studies are based on relatively limited data. This is especially the case for analyses based on a few repeated transects as they usually have substantial temporal gaps between them, making them prone to interannual variations being projected erroneously onto long-term trends (Gilbert et al., 2010). Thus, the determination of whether the oceanic content of oxygen has decreased in response to the observed global ocean warming requires not only an extension of the analysis backward in time to cover at least 30 to 40 years, it also requires a good temporal resolution in order to be able to distinguish between natural fluctuations and long term changes. This can only be achieved by combining data from a large number of different cruises and by analyzing them on a region-by-region basis (see e.g. Stramma et al. (2008), and Gilbert et al. (2010)).

Another crucial requirement for the reliable determination of long-term trends is to have an internally consistent set of data. The combination of data from a large number of sources makes this requirement particularly challenging, especially for oxygen, as there exists no certified reference material or absolute standards (Emerson et al., 1999). This internal consistency is usually achieved by applying a secondary quality control procedure to the data (Johnson et al., 2001; Key et al., 2004, 2010), i.e., data from the different cruises are compared in the deep ocean at cross-over locations resulting in the determination of adjustment factors that are then applied on a cruise-by-cruise basis (see e.g. Tanhua et al. (2010b)). While this secondary quality control does not increase the accuracy, it makes the data
suitable for long-term trend studies (Stendardo et al., 2009). Some projects such as CARINA (CAR-
bon In the Atlantic) (Key et al., 2010) and GLODAP (GLobal Ocean Data Analysis Project) (Key
et al., 2004) have already assembled a large collection of hydrographic data that were subjected to first
and secondary quality control procedures, but their temporal coverage is limited.

In this paper we augment the oxygen data from the CARINA and GLODAP data sets with selected
 cruises from the World Ocean Database 2005 (WOD05) (Boyer et al., 2006) (National Oceanographic
Data Center NODC) in order to generate an internally consistent data set for the entire North At-
lantic covering the period from 1960 until the present, i.e., covering nearly 50 years. This permits
us to reliably determine long-term trends and to investigate the causes for these trends including the
relationship with the observed warming of the ocean (Levitus et al., 2005, 2009).

We focus on the North Atlantic for several reasons. First, prior analyses of the oxygen changes in the
North Atlantic have revealed substantial changes (Johnson and Gruber, 2007; Stramma et al., 2008).
However, these analyses were spatially restricted or covered only the last 20 years. Second, the North
Atlantic is subject to substantial interannual to decadal changes in connection with the North Atlantic
Oscillation (NAO) (Visbeck et al., 2003) with potentially important implications for oceanic oxygen
(Fr¨olicher et al., 2009). Third, and finally, the North Atlantic has among the best data coverage of all
ocean basins, making it possible to reliably determine trends over an entire basin.

The longest trend analyses of oxygen in the Atlantic were conducted by Stramma et al. (2008), who
focused on the oxygen minimum zones (OMZ) of the tropical North and South Atlantic. They found
that the OMZ in these regions intensified and expanded over the last 50 years, similar to the signals
they identified in the other oceanic basins. They suggested that this could be caused by anthropogenic
climate change, especially since they found corresponding decreases also in the Pacific and Indian
Oceans. However, no formal attribution was undertaken. Long-term oxygen changes are not restricted
to the tropical Atlantic. Further north in the domain of the subpolar gyre Johnson and Gruber (2007)
reported a substantial decrease in the oxygen content of the Mode and Intermediate waters. They
attributed these changes largely to changes in the NAO, which has undergone a long-term evolution
from largely negative states in the 1960s to the late 1980s/early 1990s, but since then has decreased
again to near neutral to negative values (Hurrell et al., 2003). No connection of this loss of oxygen to
anthropogenic climate change could be made, since the analyzed data record covered only 15 years.
At the same time, model simulations predict substantial decreases in the oceanic oxygen in the North
Atlantic in response to anthropogenic climate change until the end of the century, only partially offset
by increases in some regions of the tropical Atlantic (Fr¨olicher et al., 2009). But Fr¨olicher et al. (2009)
demonstrated also that the North Atlantic is one of the regions where the natural variability of oxygen
is largest so that detection and attribution studies will be more difficult there. Here, we do not attempt
to conduct such a formal detection and attribution, but rather provide the long-term observational basis
required for such future studies.

A better understanding of long-term oxygen variations and changes in the North Atlantic may help also
to better decipher changes associated with the Meridional Overturning Circulation (MOC) (Brennan
et al., 2008) and its linkage to subpolar gyre circulation (H¨akkinen, 2001), Labrador Sea Water (LSW)
formation and spreading (e.g. van Aken et al. (2011); Yashayaev et al. (2007); Kieke et al. (2009)) and
its important role in the uptake of anthropogenic carbon (Gruber, 1998; Sabine et al., 2004; Steinfeldt
et al., 2010).
3.2 Methods

3.2.1 Data Sets

Our analysis is based on three data sets: CARINA (?), GLODAP (Key et al., 2004), and WOD05. CARINA is a collection of 98 hydrographic cruises for the Atlantic ocean (188 in total for the entire ocean) spanning 29 years (from 1977 to 2006). 81 of these cruises contain oxygen observations, all of which underwent a careful secondary quality control, resulting in the application of adjustments to 23 of them. Most of the adjustments were in between $\pm 1\%$ and $\pm 2\%$, while only five cruises needed an adjustment larger than $2\%$ (Stendardo et al., 2009). GLODAP contains 48 cruises in the Atlantic Ocean with a time span of 15 years starting from 1978. All GLODAP cruises contain high quality oxygen data that were also subjected to a secondary quality control (Key et al., 2010). CARINA and GLODAP are internally consistent, since GLODAP was used as a reference during the secondary quality control procedures of CARINA (Stendardo et al., 2009). WOD05 contains 5645 cruises in the Atlantic with at least one oxygen observation, spanning the period from 1960 to 2004. While the spatio-temporal coverage of this data set is very good, these data underwent only a relatively rudimentary primary quality control (see Boyer et al. (2006) for details), and no adjustments for cruise offsets were applied. This precludes the use of the WOD05 for trend determination without proper data selection/adjustments.

Rather than attempting to adjust the WOD05 oxygen data in toto, we used CARINA data to identify and select those cruises from WOD05 that are consistent with the CARINA oxygen data. The selection procedure consisted of a similar method used to determine the adjustments of the CARINA data set during the secondary quality control (Tanhua et al., 2010b). In detail, we computed the oxygen offsets between CARINA and WOD05 measurements on a cruise-by-cruise basis through a cross-over analysis using the MATLAB routines provided by CARINA (http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html). The results from the cross-over analysis were used to calculate the adjustment values for each cruise of the WOD05 using an inversion based on a Weighted Damped Least Square method (WDLSQ) (all the details of the methods are described in Tanhua et al. (2010b)). Only those cruises that required an adjustment of less than 1%, i.e., whose adjustment factor was between 0.99 and 1.01 were selected. All other cruises were discarded. This resulted in the identification of 184 cruises with high-quality oxygen data spanning the period 1960 to 2000. Duplicate cruises, i.e., those included in more than one of the three sources, were sub-selected with the highest priority given to CARINA and then GLODAP. In order to further extend the length of the record, we added one recent high-quality cruise conducted in 2009, i.e., Merian cruise MSM12/3 that sampled the subpolar North Atlantic.

The combined data set contains 331 cruises, 22,849 stations, and a total of 465,998 oxygen observations (251 cruises, 13,224 stations and 239,703 oxygen observation for the North Atlantic from 30\degree N to 65\degree N) spanning the period from 1960 until 2009 and with a good spatial coverage (Fig. 3.1a). CARINA and GLODAP dominate the period from 1980s to 2005, while WOD05 contributes most of the data for the period from 1980 until 1995 and also permitted us to extend the record back to 1960 (Fig. 3.1b).
Figure 3.1:  a) Map of the North Atlantic showing the stations contained in the different data sets (green for WOD05, blue for GLODAP, violet for CARINA, and red for the cruise MSM12/3). Also shown are the eight regions: LS (Labrador Sea), IS (Irminger Sea), IB (Iceland Basin), RT+WEBn (Rockall Trough and Western European Basin North), NFL (Newfoundland Basin), NAB (North American Basin), MAR (Mid Atlantic Region), and WEBs (Western European Basin South). b) Number of observations per year in the different data sets within the North Atlantic region shown in a).

3.2.2 Trend Analysis

We defined 8 regions of investigations based on basin topography and circulation pattern, i.e., the Labrador Sea (LS), the Irminger Sea (IS), the Iceland Basin (IB), the Rockall Trough together with the northern part of the Western European Basin (RT+WEBn), the North American Basin (NAB), the
Newfoundland Basin (NFL), the Mid Atlantic region (MAR) and the southern part of the Western European Basin (WEBs) (Fig. 3.1a).

The definition of such rather large regions permits us to obtain a good temporal coverage in each region, but comes at the expense of a potential aliasing effect emanating from a possible uneven distribution of the data within the region over time. We attempted to eliminate this potential aliasing by adjusting each oxygen observation in our data set to the center of the region. The spatial adjustment was determined from the gridded WOCE Global Hydrographic Climatology (Gouretski and Koltermann, 2004) by computing the difference between the oxygen concentration at the grid-point closest to the location and depth of the measurement and the mean oxygen concentration of the entire region at that depth. These adjustments ranged between $-18.1 \mu\text{mol kg}^{-1}$ and $18.7 \mu\text{mol kg}^{-1}$ (5th and 95th percentiles), while 50% of the adjustments were smaller than $0.1 \mu\text{mol kg}^{-1}$.

The trend analysis was performed on isopycnal layers on the basis of potential density ($\sigma_1$) referenced to 1000 dbar pressure and with a layer thickness of $0.1 \text{ kg m}^{-3}$ until the $32.4 \text{ kg m}^{-3}$ layer, and a thickness of $0.05 \text{ kg m}^{-3}$ until $32.5 \text{ kg m}^{-3}$. Data shallower than 100 m depth and occurring at densities lighter than the minimum density in winter time were excluded from the analysis in order to avoid seasonal signals. The winter time density at each location was taken from the World Ocean Atlas 2001 (Conkright et al., 2002). We binned the data to annual increments on each layer, in order to avoid potential aliasing effects from the fact that certain years contain many more observations than others. The resulting data distribution by layer and region (Figure S1 in the online auxiliary material) reveals overall a good temporal coverage for each analyzed $\sigma_1$ layer, but also some pronounced gaps. These gaps impact the determination of interannual variations, but our tests based on subsampling the data indicate that they are not causing major problems regarding the determination of the long-term trends.

We divided the $\sigma_1$ layers into five density horizons: Upper Water (UW) from $30.2 \sigma_1$ to $31.3 \sigma_1$, Mode Water (MW) from $31.3 \sigma_1$ to $31.8 \sigma_1$, Intermediate Water (IW) from $31.8 \sigma_1$ to $32.3 \sigma_1$, Lower Intermediate Water (LIW) from $32.3 \sigma_1$ to $32.4 \sigma_1$ and finally Labrador Sea Water (LSW) from $32.4 \sigma_1$ to $32.45 \sigma_1$. Within these layers we can identify some of the main Atlantic ocean water masses. The upper water masses characterized by thick layers of nearly uniform properties (temperature, salinity and density) (McCartney and Talley, 1982; ?) are the Mode Waters consisting of Subpolar Mode Water (SPMW) in the subpolar North Atlantic and Subtropical Mode Water (STMW) in the subtropical gyre of the North Atlantic. The SPMW, which is found throughout the supolar gyre, is characterized by densities between $\sigma_0 26.9 \text{ kg m}^{-3}$ ($\sigma_1 31.3 \text{ kg m}^{-3}$) and $\sigma_0 27.2 \text{ kg m}^{-3}$ ($\sigma_1 31.7 \text{ kg m}^{-3}$) and temperatures between $14^\circ\text{C}$ and about $11^\circ\text{C}$ (Talley et al., 2011). Thus, our MW horizon corresponds largely to SPMW. Underneath the MW lies the Intermediate Water (IW) often characterized by extrema in one or more hydrographic parameters (van Aken, 2000). These water masses include the Sub-Arctic Intermediate Water (SAIW), the Mediterranean Sea Overflow Water (MOW) and the Antarctic Intermediate Water (AAIW). Intermediate waters like the MOW and the SAIW have a mean potential density of about $\sigma_1 32.15 \text{ kg m}^{-3}$, with MOW associated with a strong salinity maximum and seen as a deep marker of subtropical influence (Johnson and Gruber, 2007). In contrast, the SAIW originates in the western boundary current of the subpolar gyre and can be considered as a deep marker of subpolar influence (Johnson and Gruber, 2007). The AAIW instead originates in the Southern Ocean and it moves northward and is brought into the northeastern North Atlantic by the North Atlantic Current.
Chapter 3. Oxygen trends over five decades in the North Atlantic

These three water masses occupy our IW horizon. The LSW density horizon corresponds exactly to the domain of the Labrador Sea Water, which is formed through deep convection in the Labrador Sea (Yashayaev et al., 2007).

The oxygen trends were computed for each isopycnal layer using a least-squares linear regression method, with the uncertainty estimated by using two standard deviations of the uncertainty in the slope. We also performed a Student-t test to determine the significance of the trend at the 95% confidence level. We run a bootstrapping analysis to check if our trends and their uncertainties are substantially impacted by our choice of annual binning. To this end, we created 1000 new timeseries for each $\sigma_1$ level with the same number of annual points as the original timeseries, but where years with more than one observation were represented by a randomly selected value rather than the mean. We then computed the trends of each timeseries and determined the median and the 95% confidence interval from the cumulative distribution of the slopes. This method gave very similar values, indicating that the trends and uncertainties computed from the annual mean oxygen for each year is robust (see Figure S2 in the online auxiliary material).

We also computed the trends and concentration changes for each watermass horizon using two separate methods. First, we used the linear trends computed for each isopycnal layer and averaged them in a weighted manner over the water mass, with the weights stemming from the volumes of the isopycnal layers that make up the five horizons. The uncertainties were determined by quadratic (Gaussian) propagation of the standard error of the trend and the significance determined by a Student-t test at the 95% confidence level. This first method assumes that the trend for each layer is statistically independent, which is reasonable since each trends is computed on the basis of completely independent data. To check upon this assumption, we alternatively determined the trend directly for the entire watermass horizon using all data within this horizon. To this end, the mean concentration on each layer was subtracted to form an anomaly, which were then combined across the entire horizon for the trend analysis. This alternative method to determine trends over entire density horizons yielded statistically indistinguishable results from those obtained by the first method. The numerical values reported in this paper come from the first method.

To further check the robustness of the linear regression trends, we also determined the difference between the mean oxygen value of all data from 1990 to 2005 and the mean value of all observations from 1960 to 1975. This method is less sensitive to the values at the beginning or end of the timeseries, but requires a relatively even coverage of the data within these two 15 years periods. This is fulfilled for almost all the regions except the LS and some shallower layers (Figure S1). This analysis gave on average slightly smaller trends with time, but fully support our linear regression-based results (Figure S3 in the online material). As a final check to test the robustness of the trends we determined the Theil-Sen based trend that computes the trend by calculating the median of the slopes between all data pairs (results of this estimate is shown in Figure S4 in the online material). This also gave very similar results to those inferred from the standard linear regression model.

3.2.3 Temperature, $O_2^{sat}$, AOU, and $O_2^*$

In order to determine the potential processes driving the changes in oxygen, we also analyzed trends in the saturation concentration of $O_2$, i.e., $O_2^{sat}$, trends in the apparent oxygen utilization (AOU),
3.2. Methods

and trends in the quasi-conservative tracer O$_2$ (Gruber et al., 2001). The analysis of trends in O$_{2sat}$ permits us to assess the role of heat exchange at the air-sea surface, as this affects the saturation concentration and ultimately the uptake/loss of oxygen at the sea-surface. We compute O$_{2sat}$ from the concurrently measured temperatures and salinity using the formulation of Weiss (1970). Trends of −AOU (−AOU = O$_2$ − O$_{2sat}$) indicate the contribution of processes other than warming/heating on the trend in oxygen, i.e., primarily the rate of oxygen consumption from the remineralization of organic matter, i.e., the biological driver, and the rate of transport and mixing of the water mass. Thus we separate the trends into the following two contributors:

$$\frac{dO_2}{dt} = \frac{dO_2}{dt}|_{bio,trsp} + \frac{dO_2}{dt}|_{heat} = \frac{d(-AOU)}{dt} + \frac{dO_{2sat}}{dt}$$ (3.1)

An important caveat in this separation is the assumption that surface ocean oxygen fully equilibrates with the atmosphere in response to heating/cooling of the surface. This does not always occur, particularly not in the high-latitudes during winter time (Ito et al., 2004). As a result, one would tend to overestimate the heat flux driven component trend and underestimate the trend component stemming from biology and/or transport/mixing.

A corollary separation can be achieved by analyzing the trend in the quasi-conservative tracer, O$_2$ = O$_2$ − r$_{O_2:PO_4}$ PO$_4$, where r$_{O_2:PO_4}$ is the oxygen to phosphorus ratio of biological uptake/release. O$_2$ is a tracer that reflects the O$_2$ gained or lost by a water parcel through air-sea gas exchange, irrespective of whether this exchange occurs as a result of biological consumption and production of O$_2$ in the surface ocean or whether it is the result of heating and cooling the surface (Gruber et al., 2001; Keeling and Garcia, 2002). This second separation thus consists of the following:

$$\frac{dO_2}{dt} = \frac{dO_2}{dt}|_{gasex} + \frac{dO_2}{dt}|_{no-gasex} = \frac{dO_{2}^*}{dt} + \frac{(r_{O_2:PO_4} \cdot PO_4)}{dt}$$ (3.2)

where the “no-gasex” component includes all processes at the surface and interior that are not associated with the exchange of O$_2$ across the air-sea interface. This is primarily biology and transport and mixing. In contrast, O$_2^*$, i.e., the “gasex” component corresponds directly to the amount of O$_2$ that the ocean is losing or gaining from the atmosphere, i.e., it is that part of the marine O$_2$ that leaves an imprint on atmospheric oxygen (Gruber et al., 2001; Keeling and Garcia, 2002). The biological production and consumption at the surface add or remove oxygen from the water that can create an air-sea disequilibrium of oxygen and thus lead to air-sea gas exchange (Gruber et al., 2001) that consequently affect the O$_2^*$. A reduction of the transport of this biologically produced oxygen from the surface into the ocean’s interior would tend to cause a larger loss of this biological oxygen to the atmosphere, and thus causing a reduction in O$_2^*$. An increase of this transport would tend to increase O$_2^*$. However, cooling and warming at the surface have also the potential to alter O$_2^*$ strongly since they can cause an air-sea disequilibrium of oxygen as well.

We used the phosphate observations from our data sets to compute O$_2^*$. While a secondary quality control was undertaken for phosphate in the GLODAP and CARINA data sets, no additional checks were performed on the phosphate data from WOD05. As a result, we have less confidence in the long-term trends of O$_2^*$. The analysis of the O$_2^*$ is also hampered by the fact that we lack phosphate data for many cruises that have O$_2$ data. This is especially the case for many of the earlier cruises,
therefore restricting the length of the O₂ trends substantially. We therefore will be using O₂ trends in a qualitative manner only.

3.2.4 Inventory Changes

We computed the changes in the oxygen (and heat) inventories by multiplying the rates of change with the volume of the respective water mass on each analyzed σ₁ layer. The volumes were determined from the WOCE Global Hydrographic Climatology (Gouretski and Koltermann, 2004), thereby neglecting changes in the volumes of the water mass or layer under consideration. To compute inventories by depth intervals, we first transformed the rates of change by σ₁ layer to rates of change by depth, and then integrated them vertically. The transformation from σ₁ to depth was also based on the WOCE Global Hydrographic Climatology.

3.3 Long-term Oxygen Trends

3.3.1 Overview

We find substantial long-term changes in the oxygen concentration along isopycnal layers over the last 49 years starting from 1960 for each region of the North Atlantic (Fig. 3.2). Because of the sparsity of data and the elimination of data above the winter time outcropping density, some regions do not have estimates for all isopycnal layers (Fig. S1 in the online material).

Our results reveal that the UW (which can be identified only in the four southern regions of the North Atlantic), has lost oxygen in all four regions with a maximum of \(-5.2 \pm 3.4 \mu\text{mol kg}^{-1} \text{decade}^{-1}\) in the NFL region (Fig. 3.2, orange curve). Also the MW has lost oxygen especially in the northern and eastern regions (RT+WEBn and WEBs), with a maximum of \(-5.7 \pm 3.9 \mu\text{mol kg}^{-1} \text{decade}^{-1}\) in the RT+WEBn region (yellow curve in Fig. 3.2). At the same time, the MW in the southwestern regions (NAB, NFL and MAR) has gained oxygen with rates as large as \(5.5 \pm 3.9 \mu\text{mol kg}^{-1} \text{decade}^{-1}\) in the NAB region. Also the IW layer shows a distinct east-west difference in trends. In the eastern part of the North Atlantic (IB, RT+WEBn, MAR and WEBs) oxygen has decreased on average over the past 50 years with a maximum decrease observed in the IB region of \(-7.4 \pm 2.9 \mu\text{mol kg}^{-1} \text{decade}^{-1}\). On the other hand, IW has increasing trends in the northwestern and western part of the basin (LS, NAB), particularly in the denser classes of this horizon. In contrast, the LIW and LSW horizons show increases in the oxygen concentration in all regions with a maximum in the IB (2.1 \(\pm\) 1.9 \(\mu\text{mol kg}^{-1} \text{decade}^{-1}\)) and in the WEBs region (3.3 \(\pm\) 1.9 \(\mu\text{mol kg}^{-1} \text{decade}^{-1}\)) respectively. Overall, we find a complex pattern of trends with the upper layers of the ocean, corresponding to the domains of the UW, MW and IW horizons, having lost oxygen, and with the deeper layers, representing the LIW and LSW horizons having gained oxygen. The weighted average loss over the UW, MW, and IW water mass horizons is \(-5.0 \pm 1.7 \mu\text{mol kg}^{-1}\) for the last 49 years. The deeper layers (LIW and LSW) gained nearly the same amount of oxygen over this period, i.e., \(5.5 \pm 2.6 \mu\text{mol kg}^{-1}\).
Figure 3.2: Isopycnal oxygen trends from 1960 through 2009 for the 8 analyzed regions. The colors of the lines correspond to the colors of the regions. The shading around each lines represents the trend ± 2 standard deviation (2σ). The gray boxes represent the $\sigma_1$-based density horizons in defined in this study: UW (Upper Water), MW (Mode Water), IW (Intermediate Water), LIW (Lower Intermediate Water), and LSW (Labrador Sea Water).
3.3.2 Potential Causes

The separation of the trends into a part driven by changes in solubility and into a part driven by biology and circulation/ventilation, i.e., $O_{2}^{sat}$ and AOU, (see eq. (1)) reveal that both sets of processes contribute to them, with the AOU contribution overall dominating (Figs. 3.3 and 3.4).

Similar to the oxygen trends, the $-\text{AOU}$ trends show negative values in the domain of the UW, IW and MW, and positive values in the MW in the southern regions and in the LIW and LSW in all the regions (Fig. 3.3). One main difference is found on the shallower isopycnal layers in the southern regions, where the decreases in oxygen are larger than those in $-\text{AOU}$. In the NFL, for example, $-\text{AOU}$ contributes only (a not statistically significant) $-3.3 \pm 3.7 \mu\text{mol kg}^{-1} \text{ decade}^{-1}$ to the overall oxygen decrease of $-5.2 \pm 3.4 \mu\text{mol kg}^{-1} \text{ decade}^{-1}$. The most important differences exist on the LIW and the LSW horizons, where the oxygen increase is not associated with a trend in $-\text{AOU}$.

The trends in oxygen solubility dominate the oxygen trends only in a few areas (Fig. 3.4), i.e., in the upper isopycnal horizons in the southern regions (NFL and MAR) where the decrease in oxygen is largely caused by a decrease in oxygen solubility, and in the deeper isopycnal horizons where increasing oxygen solubility explains most of the observed increase in oxygen. The strongest changes in oxygen solubility are found in the MW and IW horizons in the NFL and MAR regions with a maximum value in the NFL of $-5.4 \pm 4.1 \mu\text{mol kg}^{-1} \text{ decade}^{-1}$. This strong negative trend is, however, compensated by an even stronger positive trend in $-\text{AOU}$, so that the overall trend is slightly positive.

**Figure 3.3:** As Figure 3.2, but for the negative of the apparent oxygen utilization (-AOU).
3.3. Long-term Oxygen Trends

Figure 3.4: As Figure 3.2, but for the oxygen saturation concentration, $O_2^{sat}$.

When averaged over entire watermass horizons, robust and largely significant $O_2$ trends emerge for many of the analyzed regions and water masses (Fig. 3.5). In this plot and in the related Fig. 3.6, the trends were converted to concentration changes over the 49 years of the records. Statistically significant concentration changes are represented with filled circles, the not significant ones are plotted with open circles, and regions with insufficient data are shaded in grey. We use these water horizon averaged values for our subsequent detailed discussions.

Upper Water horizon

The substantial long-term decrease in oxygen of more than 10 $\mu$mol kg$^{-1}$ observed in the Upper Water horizon and especially in the central regions of the southern North Atlantic (NFL and MAR) is largely due a reduction in solubility stemming from the concurrent warming (Fig. 3.5a and b). This reduction is enhanced by the negative trend in $-AOU$ (Fig. 3.5c), which is by itself not statistically significant, but nevertheless increases the trend by several ten percent. This reduction in $-AOU$ (increase in AOU) is likely primarily caused by the warming induced decrease in the ventilation of this particular isopycnal horizon, although a biological contribution cannot be excluded. The $O_2^*$ changes (Fig. 3.6a) are even more negative in most regions of this isopycnal horizon, indicating that most of the oxygen reduction was transmitted into the atmosphere, increasing oxygen there.
Figure 3.5: Weighted mean $O_2$ concentration changes over the last 49 years for the five horizons and their drivers. The first column (a, d, g, j and m) show the changes in oxygen, while the second (b, e, h, k, and n) and third columns (c, f, i, l and o) show the changes induced by solubility (represented by the $\Delta O_2^{\text{sat}}$) and by changes in circulation/ventilation and remineralization (represented by the $-\Delta AOU$), respectively. The rows show the results for the different water masses: UW: a, b, c; MW: d, e, f; IW: g, h, i; LIW: j, k, l; LSW: m, n, o). Statistically significant concentration changes are represented with filled circles, while the not significant ones are plotted with open circles.
Figure 3.6: As Figure 3.5, but for the gas-exchange component of oxygen, i.e., $O_2^*$. Regions with insufficient data are shaded in grey.

Mode Water horizon

The oxygen changes in the Mode Water horizon display a clear separation between a large decrease in oxygen (up to $-18 \mu$mol kg$^{-1}$) in the eastern and northern regions of the North Atlantic, and a strong increase (about $20 \mu$mol kg$^{-1}$) in the southwestern regions, especially in the NAB region (Fig 3.5d). These changes are almost entirely driven by the changes in $-\text{AOU}$ (Fig. 3.5f), with solubility dampening the circulation and biology-driven changes in the south-central regions (NFL and MAR) (Fig. 3.5e).

The long-term decreases in the eastern and northern regions are rather steady in time (Fig. 3.7), with a hint of a possible acceleration since the early 1990s. This permits us to put these changes in the context of the study of Johnson and Gruber (2007) who investigated the oxygen decrease in the SPMW observed at $20^\circ$W between 1988 and 2003. These authors linked the oxygen loss in this water mass to variations in the NAO with the observations in 1993 reflecting conditions after a period of relatively high NAO, and those in 2003 reflecting conditions after a period of much lower NAO. This shift in NAO caused the SPMW to be colder, fresher, denser, and hence containing more oxygen in 1993, and warmer, saltier, lighter and hence containing less oxygen in 2003. They also identified a substantial contribution of $-\text{AOU}$ to the changes, which they suggested to be primarily the result of a northwest movement of the subpolar gyre and a corresponding shift in the position of the NAC and the associated front between the higher and lower oxygen flavors of SPMW. While our oxygen data concur with the oxygen decrease between the early 1990s and early 2000s (Fig. 3.7), they indicate almost no contribution from solubility changes. Instead, our data attribute the oxygen reduction to a trend in $-\text{AOU}$, irrespectively of whether the change corresponds to the entire period or just to the period from 1993 to 2003. Thus, while the longer-term perspective confirms the conclusions of Johnson and Gruber (2007) with regard to the role of $-\text{AOU}$, our new data suggest no substantive contribution from solubility.

Johnson and Gruber (2007) argued that given the corresponding changes in temperature, salinity, potential vorticity and the depth structure of the observed oxygen changes, the reduction in $-\text{AOU}$ likely
Figure 3.7: Timeseries of trends in oxygen and its components for selected regions of the mode-water density horizon. The first row, i.e., panels a), b) and c) show trends for $O_2$, the second row, i.e., panels d), e) and f) those for $O_{sat}^2$, and the third row, i.e., panels g), h) and i) those for $O_*^2$. Actually plotted are the anomalies relative to the long-term mean on each of the isopycnal layers that contribute to the mode-water density horizon. The first column, i.e., panels (a), d) and g) depict the results for the RT+WEBn region. The second column, i.e., panels b), e), and h) depict the results for the WEbS region. The third column, i.e., panels c), f) and i), depict the results for the NAB region. The symbols are the anomaly from the median value of the linear trend for each isopycnal layer that forms the MW horizon, while the thick line is the linear trend. In the lower left corner is the trend with the uncertainty in $\mu$mol kg$^{-1}$ decade$^{-1}$. 
does not come from an increase in the rate of biological oxygen demand, but is more likely a result of circulation and ventilation changes. Our results support this conclusion, although we lack the concomitant observations to separate the role of biology clearly from the role of circulation. Nevertheless, the general decrease in $O_2^*$ in the northeastern North Atlantic and especially in the RT+WEBn region (Fig. 3.6b) would support an important role of ventilation, referred here to all processes supplying atmospheric $O_2$ to the ocean interior including air-sea gas exchange and the transport of $O_2$ across the base of the surface mixed layer. This is because in the absence of cooling or warming, one could explain all changes by invoking a long-term trend toward enhanced stratification, which tends to reduce $O_2^*$, and also tends to increase the residence time of waters on this isopycnal horizon with regard to the surface, explaining the concomitant reduction in $-\text{AOU}$ and oxygen.

In the southern part of the southeastern North Atlantic (WEBs), however, we observe a slight increase (although not significant) of $O_2^*$ and decrease in the oxygen. $O_2^{sat}$ did not change, while $-\text{AOU}$ decreased. In this case, the oxygen changes are likely driven by changes in remineralization and/or circulation alone without much contribution from the gas-exchange.

The southwestern and southcentral regions of the North Atlantic (MAR, NFL and NAB) exhibit a strong positive trend in $-\text{AOU}$ (Fig. 3.5f), suggesting a strong increase in ventilation/circulation and/or a decrease in biological consumption of oxygen. Warming in the MAR and NFL regions reduce the $-\text{AOU}$-driven trend substantially (Fig. 3.5e), causing the overall trend to be statistically not significant (Fig. 3.5d). No such dampening effect exists in the NAB region, leading to a substantial and significant oxygen increase there. The absence of significant changes in $O_2^*$ suggests that little $O_2$ was exchanged with the atmosphere, so that the additional $O_2$ in the interior must have other sources. A strong reduction of biological oxygen demand can quite likely be excluded, since in such a case, one would expect a strong decrease in oxygen demand throughout the water column with the strongest reduction occurring in the upper ocean. This is not the case since $-\text{AOU}$ shows little trend in the UW horizons in the southwestern and southcentral regions (Fig. 3.5c). This leaves stronger ocean circulation/ventilation as the primary candidate for explaining the increase in oxygen in the mode waters of the southwestern North Atlantic.

**Intermediate Water horizon**

The waters of the IW horizon show a clear east-west difference in their oxygen trends, with significant decreases of the order of $-4$ to $-16$ $\mu$mol kg$^{-1}$ in the entire central and eastern North Atlantic, and small and insignificant increases in the western regions (Fig. 3.5g). This east-west difference is entirely driven by the trends in $-\text{AOU}$ (Fig. 3.5i) while the solubility-driven trends modify the magnitude somewhat in the central Atlantic (Fig. 3.5h). The trends are overall similar to those observed in the overlying mode waters, although generally weaker (Fig. 3.5d-f). What differs, however, are the trends in $O_2^*$ (Fig. 3.6), where the IW waters show nearly everywhere an increase in $O_2^*$, albeit not a significant one. Thus gas-exchange appears to have a small positive impact on oxygen on this horizon. Using the same argument as above regarding the unlikely role of biology in causing the $-\text{AOU}$ and hence the oxygen changes, this leaves ocean circulation as the most likely candidate for explaining the differential trends in oxygen in the intermediate waters.
Chapter 3. Oxygen trends over five decades in the North Atlantic

Figure 3.8: As Figure 3.7, but for selected regions for the intermediate water horizon. Shown are the results for the IB region (panels a), d) and g)), the WEBs region (panels b), e), and h), and the MAR region (panels c), f) and i).

Johnson and Gruber (2007) reported also oxygen decreases for the intermediate waters in the eastern North Atlantic between 1993 and 2003. Our data confirm this finding and suggest that this decrease is actually just a part of a much longer trend, spanning the entire period from the early 1960s to the present (Fig. 3.8). Johnson and Gruber (2007) interpreted the changes in this density range also in the context of the shifts in the NAO with cold, fresh (and high oxygen) intermediate waters of northwestern origin being replaced by warmer, saltier, and less oxygenated intermediate waters of more southern origin (MOW and AAIW). Our slight negative trend in oxygen solubility in the WEBs region support this interpretation, although the overall oxygen trend in this region suggest a much stronger forcing from −AOU. This suggests that the stronger northward penetration of MOW and AAIW dominated intermediate waters might have been a process that has occurred since the 1960s.

Lower intermediate and Labrador Sea Water horizons

In contrast to the overlying water masses, the waters of the LIW and LSW horizons exhibit an increase in oxygen nearly throughout the entire North Atlantic (Fig. 3.5j, m). Most of this increase is driven by an increase in oxygen solubility caused by the long-term cooling of these waters (Fig 3.5k, n).
The contribution of $-\text{AOU}$ is generally not statistically significant, but nevertheless enhances the solubility-driven signal in most regions (Fig 3.5i, o). The LIW has a particular strong increase in the northeastern regions (IB and RT+WEBn) with increases in oxygen as large as 11 $\mu\text{mol kg}^{-1}$. The LSW shows the strongest increases in the northwestern and southeastern basin, also with increases of the order of 12 $\mu\text{mol kg}^{-1}$.

The long-term increase in oxygen in the LIW and LSW horizons is mostly determined by the increase in oxygen saturation (decrease in temperature) between the 1960s and the 1990s (Figure 3.9), while the trends have flattened thereafter. This is in agreement with the results of Dickson et al. (2002), who described that from 1966 to 1992 there was an overall cooling of the entire water column of the Labrador Sea. This is a consequence of an intensification of winter-time convection in the Labrador Sea over this period, which leads to the formation of cold, fresh, well oxygenated waters. Hydrographic time series reveal two periods of intensified LSW production, from 1972 to 1976, and from the late 1980s to 1997 (McCartney and Talley, 1982; Wallace and Lazier, 1988; Sy et al., 1997). This evolution brought deepening convection and ultimately formed LSW that was fresher, colder, deeper and denser than at any other time in history of deep measurements there (Dickson et al., 2002). The intense production of well oxygenated waters led also to a substantial increase in $O_2^*$ in the LIW and

![Figure 3.9: As Figure 3.7, but for selected regions for the Labrador Sea Water horizon. Shown are the results for the LS region (panels (a, d) and g)), the IB region (panels b), e), and h), and the WEBs region (panels c), f) and i).](image-url)
LSW horizons (Fig. 3.6), although the phosphate data are sparse and often of too low quality to draw more quantitative conclusions. Since the late 1990s, winter time convection has been relatively steady and even began to decrease recently (Lazier et al., 2002). This led to a slight warming of the LSW in the Labrador Sea as seen by the small downward trend in the oxygen saturation in this region (Fig. 3.9) (Lazier et al., 2002).

These signals produced locally in the LS region are then transported into the other regions of the North Atlantic along the circulation path of the LSW leading to a relatively homogeneous distribution of the trends throughout the North Atlantic. Nevertheless, the finite spreading time from the Labrador Sea to the other regions leads to deviations, particularly in how the recent cessation of the trend in the Labrador Sea is shared in the other regions. Spreading times from the Labrador Sea are about 6.5 years to the western Mid Atlantic Ridge, 7.5 years to the North Atlantic’s eastern side (Koltermann et al., 1999; Kieke et al., 2009), about 4–5.5 years to the Western European Basin (Sy et al., 1997), about 5 years to the Icelandic Basin (Yashayaev et al., 2007), and about 0.5–2 years to the Irminger Sea (Sarafanov, 2009). Considering this time lapse the signal of increasing oxygen with decreasing temperature until the 1990s and vice versa after the late 1990s can actually be seen in the Irminger Sea but gets attenuated and lost in regions further to the south (Fig. 3.9b and c). The relatively quick transfer of the Labrador Sea water properties into the northeastern North Atlantic is likely the reason why Johnson et al. (2005) saw only relatively small changes in oxygen along 20°W between 1988 and 2003.

### 3.3.3 Climate change versus NAO

Are the oxygen changes we have identified over the past five decades in the North Atlantic already a manifestation of anthropogenic climate change or are they a result of long-term trends in natural modes of climate variability, such as the North Atlantic Oscillation? Without a formal detection and attribution process, we cannot give a definite answer, but our detailed analysis of the drivers underlying the trends provide us a basis for a preliminary assessment.

The NAO represents the main mode of interannual atmospheric variability in the North Atlantic. It is characterized by positive or negative phases that are associated with corresponding changes in wind stress, wind stress curl, and heat and freshwater fluxes (Visbeck et al., 2003). The NAO has a substantial influence on the rate and intensity of deep convection in the Labrador Sea, and the rate of formation of mode waters (Dickson et al., 2002). More precisely, during periods of a positive NAO state, the oceanic heat loss in the winter is intensified in the subpolar North Atlantic, while this loss is reduced in the subtropical North Atlantic. This create a negative temperature anomaly in the subpolar gyre and a positive temperature anomaly over most of the western subtropical gyre (Visbeck et al., 2003). Also the mean path of the North Atlantic current changes in association with the NAO, with positive phases characterized by an intensification and southeastward expansion of the subpolar gyre. During negative phases, generally the opposite changes occur.

During the last 50 years the NAO index evolved from strong negative values in the late 1960 to the early 1970s to near neutral values during the late 1970s until late 1980s. Then in the late 1980s, the NAO index entered a prolonged period where it remained in its strongly positive phase, which lasted until 1995. Thereafter, the NAO index started to decrease to lower positive and sometime negative
values. This decreasing phase is relatively recent, so that the trend of the NAO index over the past 50 years is still positive.

On the base of what is known about the impact of the NAO on the North Atlantic’s temperature, ventilation and circulation, many of the oxygen changes we identified in our study can be related to the long-term trend in NAO.

The primarily ocean warming-driven decreases in oxygen in the Upper Waters in the south-central regions of the North Atlantic (NFL and MAR), can be linked to the trend toward more positive phases of the NAO, which caused a warming of the northern subtropical gyre. The reduced $O_2$ concentration in the mode water horizon can be either driven by the reduction in mode water formation in the North Atlantic due to the trend in NAO and the associated reduction in wind-stress and buoyancy

\[ \Delta[O_2] = \text{Solubility} \Delta[O_2]_{\text{sat}} + \text{Circulation/Remineralization} -\Delta[AOU]. \]

Figure 3.10: As Figure 3.5, but for vertically and temporally integrated changes in oxygen and in its components, i.e., $\Delta O_2^{\text{sat}}$ and $-\Delta AOU$. 
forcing could explain the strong \(-\)AOU and \(O_2\) trends in the eastern North Atlantic, which are likely ventilation driven. The same NAO-driven process can explain the circulation-driven reduction in the intermediate water horizon in the eastern North Atlantic. And finally, it has been already well established, that the strong cooling and hence the increase in oxygen solubility and oxygen in the lower intermediate and Labrador Sea water are a consequence of the long-term trend in the NAO.

But there are also some aspects where it is unclear whether the NAO is the main driver. First, we can only provide a tentative link to the NAO when attempting to explain the strong \(-\)AOU driven increase in the oxygen content of the mode waters of the southwestern regions, which we interpreted to be primarily caused by enhanced circulation. One possible explanation is that this increase is connected to the onset of stronger convective activity in the Labrador Sea, which enhanced the formation of well oxygenated water in the density range of MW, which then pushed southward across the Great Banks into the southwestern region. At the same time, periods of high NAO are usually associated with low rates of subtropical mode water formation (Joyce et al., 2000), which produces waters of lower density than our MW horizon, but may still influence our trends. Second, it is unclear why the intermediate waters of the western part of the North Atlantic show such a differing trend from those in the east, and third, we have difficulties to bring into agreement the relative contribution of changes in circulation and changes in ventilation to explain the changes in the mode and intermediate waters.

The latter question is related to the interpretations provided by Johnson and Gruber (2007), who emphasized the role of circulation changes in explaining the oxygen changes in the subpolar mode waters between 1993 and 2003. They argued that much of the change they identified could be explained by a northwestward movement of the North Atlantic current associated with the transition from a high to a low NAO state, permitting low oxygen waters to penetrate further north in the eastern side of the Atlantic. This would imply that the oxygen would have been even lower than today in the 1960s, when the NAO was lower compared to today. This is clearly not the case, as the mode waters show a substantial loss of oxygen from 1960 until today, and the same is true for the intermediate waters. This means that either the circulation changes are less important than ventilation or that NAO unrelated factors are the dominant driver for the oxygen changes in the mode waters. One possible explanation is that the northwestward/southeastward shifts of the North Atlantic current occurs in a manner unrelated to the NAO, but rather in response to changes in the wind stress curl over the North Atlantic, as recently suggested by Häkkinen et al. (2011). They showed that these shifts occurred roughly every 15 years, with the most recent period of a northwestward shift and associated enhanced northward penetration having taken place between the early 1990s and the early 2000s, i.e., during the period analyzed by Johnson and Gruber (2007). However, no long-term trend exists in these shifts so that they cannot explain the 50 years trends, although they likely contribute to the fluctuations around the linear trends over this period. In particular, they may contribute to the acceleration of the decrease in oxygen in the mode waters of the eastern regions seen after 1990s.

We cannot assess with certainty whether any of these NAO unrelated oxygen changes are a manifestation of anthropogenic climate change, but we note that model simulations up to the end of this century suggest a relatively homogeneous deoxygenation of the North Atlantic in response to climate change. This means that some of the oxygen decreases in the upper three horizons could be related to climate change, but it is rather unlikely that the oxygen increases in the western part of the basin in the mode and intermediate water horizons are a result of climate change.
### Table 3.1: $O_2$ inventory changes, heat content changes and Volumes over the five water masses horizons discussed in this study for each region. In bold are the results that are statistically significant.

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<th>$O_2$ inv. changes</th>
<th>LS (Tmol)</th>
<th>IS</th>
<th>IB</th>
<th>RT+WEBn</th>
<th>NFL</th>
<th>NAB</th>
<th>MAR</th>
<th>WEBs</th>
<th>Tot.</th>
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</thead>
<tbody>
<tr>
<td>UW</td>
<td>-1.6 ± 1.9</td>
<td>-11.2 ± 6.1</td>
<td>1.6 ± 3.3</td>
<td>7.5 ± 4.0</td>
<td>4.6 ± 5.9</td>
<td>-14.4 ± 4.7</td>
<td>-13.0 ± 11.2</td>
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</tr>
<tr>
<td>MW</td>
<td>8.4 ± 3.8</td>
<td>-14.9 ± 6.3</td>
<td>-9.4 ± 7.1</td>
<td>-0.6 ± 4.5</td>
<td>4.4 ± 7.9</td>
<td>-12.3 ± 4.7</td>
<td>-4.0 ± 9.6</td>
<td>-36.1 ± 15.2</td>
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</tr>
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<td>IW</td>
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<td>10.3 ± 9.0</td>
<td>9.7 ± 8.2</td>
<td>0.7 ± 13.1</td>
<td>0.6 ± 16.9</td>
<td>3.0 ± 10.0</td>
<td>5.2 ± 5.2</td>
<td>31.8 ± 30.1</td>
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<tr>
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<td>2.7 ± 3.3</td>
<td>5.3 ± 3.2</td>
<td>2.3 ± 3.0</td>
<td>5.1 ± 9.6</td>
<td>5.4 ± 4.8</td>
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<td>Heat Content (10^24 J)</td>
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<td>0.10 ± 0.05</td>
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</tr>
<tr>
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<td>0.01 ± 0.03</td>
<td>0.01 ± 0.03</td>
<td>0.01 ± 0.03</td>
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<td>0.01 ± 0.03</td>
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<td></td>
</tr>
<tr>
<td>IW</td>
<td>-0.02 ± 0.02</td>
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<td>-0.02 ± 0.02</td>
<td>-0.02 ± 0.02</td>
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</tr>
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<td>-0.40 ± 0.18</td>
<td>-0.26 ± 0.17</td>
<td>-0.11 ± 0.26</td>
<td>-0.14 ± 0.37</td>
<td>-0.11 ± 0.15</td>
<td>-0.19 ± 0.16</td>
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<td>-0.15 ± 0.03</td>
<td>-0.15 ± 0.08</td>
<td>-0.06 ± 0.05</td>
<td>-0.12 ± 0.12</td>
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<td>-0.28 ± 0.16</td>
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<td>2.4</td>
<td>3.8</td>
<td>7.3</td>
<td>8.9</td>
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<tr>
<td>IW</td>
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<td>3.6</td>
<td>9.3</td>
<td>11.4</td>
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<td>8.1</td>
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<td>4.9</td>
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<td>9.0</td>
<td>7.8</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>UW</td>
<td>-16.5 ± 8.2</td>
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<td>-3.7 ± 2.2</td>
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<td></td>
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</tr>
<tr>
<td>MW</td>
<td>-9.4 ± 17.1</td>
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<td>6.5 ± 13.7</td>
<td>19.3 ± 10.2</td>
<td>6.1 ± 7.9</td>
<td>-15.7 ± 5.1</td>
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</tr>
<tr>
<td>IW</td>
<td>9.7 ± 15.3</td>
<td>-4.4 ± 8.1</td>
<td>-15.6 ± 6.6</td>
<td>-8.1 ± 6.1</td>
<td>-1.3 ± 8.9</td>
<td>5.3 ± 9.4</td>
<td>-12.7 ± 4.9</td>
<td>-3.9 ± 3.5</td>
<td>-6.0 ± 2.5</td>
</tr>
<tr>
<td>LSW</td>
<td>2.1 ± 9.8</td>
<td>-0.3 ± 7.9</td>
<td>10.5 ± 9.2</td>
<td>10.9 ± 9.2</td>
<td>0.9 ± 17.2</td>
<td>0.5 ± 13.8</td>
<td>2.5 ± 8.3</td>
<td>7.5 ± 7.6</td>
<td>4.1 ± 3.9</td>
</tr>
<tr>
<td>LSW</td>
<td>10.2 ± 9.1</td>
<td>5.8 ± 7.2</td>
<td>9.0 ± 5.4</td>
<td>4.5 ± 6.0</td>
<td>5.8 ± 6.5</td>
<td>5.5 ± 10.4</td>
<td>6.8 ± 6.0</td>
<td>12.3 ± 8.0</td>
<td>7.5 ± 2.9</td>
</tr>
</tbody>
</table>
Chapter 3. Oxygen trends over five decades in the North Atlantic

Table 3.2: O\textsubscript{2} inventory changes, heat content changes and volumes over the first 700 m depth and from 700 m to 2750 m for each region. In bold are the results that are statistically significant.
3.4 Changes in oxygen inventory and its relationship to heat uptake

Summing over all regions and over the upper three density horizons (UW, MW, and IW), the upper North Atlantic has lost $-58 \pm 20 \text{Tmol}$ of oxygen between 1960 and 2009 (Table 3.1). This loss is offset by a gain of $70 \pm 34 \text{Tmol}$ in the two deeper horizons (LIW and LSW), resulting in an insignificant total gain across all considered density horizons of $12 \pm 40 \text{Tmol}$. The mean oxygen changes are not very different in the upper and lower horizons of the North Atlantic, but the substantially larger volume of the LIW and LSW horizons ($124 \times 10^{14} \text{m}^3$ versus $99 \times 10^{14} \text{m}^3$), leads to the net gain of oxygen over all horizons. The spatial distribution of the oxygen inventory changes follows largely that of the oxygen concentration (compare Fig. 3.10 with 3.5), but with distinct shifts in emphasis on a regional scale induced by the volume weighting.

We computed also the changes in oxygen and oxygen inventory as a function of depth by projecting the isopycnally-determined oxygen trends onto a depth coordinate. From 100 m down to 700 m, corresponding largely to the depth range occupied by the UW, MW and IW horizons, the mean oxygen loss between 1960 and 2009 amounts to $-5.1 \pm 2.9 \mu \text{mol kg}^{-1}$ giving a total loss of $-29.0 \pm 16.3 \text{Tmol}$ (Table 3.2). In contrast, from 700 m to 2750 m oxygen increased, on average by $2.4 \pm 1.9 \mu \text{mol kg}^{-1}$, yielding a total oxygen gain of $44.9 \pm 36.6 \text{Tmol}$ (Table 3.2). The relative errors of these depth-based inventories are larger due to the uncertainties associated with the projection from density to depth.

Thus, overall the North Atlantic seems to have gained a small and statistically insignificant amount of oxygen over the past nearly 50 years. But this hides the fact that over this period, oxygen has been redistributed strongly between the upper and lower layers of the North Atlantic.

3.4.1 $O_2$ loss to heat gain ratio

Model studies (Plattner et al., 2002; Matear and Hirst, 2003; Oschlies et al., 2008; Frölicher et al., 2009), theoretical considerations based on the spatial distribution of oxygen (Gruber et al., 2001) and observationally-based estimated using the seasonal cycle of the air-sea fluxes of oxygen (Najjar and Keeling, 2000; Keeling and Garcia, 2002) suggested that changes in the oceanic $O_2$ content are strongly tied to changes in the oceanic heat content. As explained earlier, this is because solubility and other factors altering oxygen tend to enhance each other, leading to a larger change in oxygen concentration than predicted based on oxygen solubility alone. Based on the relationship of $O_2^*$ with temperature and seasonal cycle of oxygen and heat fluxes, Keeling and Garcia (2002) computed a global mean ratio of approximately $-5 \text{nmol J}^{-1}$ for thermocline waters with a range of $-2$ to $-10 \text{nmol J}^{-1}$, depending on region and mean temperature. Models run under strong climate change scenarios gave ratios between $-5$ to $-6 \text{nmol J}^{-1}$ (Keeling et al., 2010). Our data gives us now the opportunity to determine this ratio for the first time from in-situ trends.

Using our temperature data to determine the heat content changes over the eight regions, we obtain for the upper three water horizons a $O_2$ loss to heat gain ratio of $-4.6\pm 2.8 \text{nmol J}^{-1}$ (Table 3.3). This value is close to the mean estimate of Keeling and Garcia (2002) for thermocline waters. The $O_2$/heat
Table 3.3: $O_2$/Heat ratios for the three water masses and the ratios derived from the effect of the solubility alone by using the $O_2$ saturation in third column.

<table>
<thead>
<tr>
<th></th>
<th>$O_2$/Heat ratio</th>
<th>$O_2$/Heat ratio sol. alone</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-700 m</td>
<td>$-4.8 \pm 4.3$</td>
<td>$-1.6$</td>
</tr>
<tr>
<td>700-2750 m</td>
<td>$-2.0 \pm 1.9$</td>
<td>$-1.9$</td>
</tr>
<tr>
<td>UW-MW-MW</td>
<td>$-4.6 \pm 2.8$</td>
<td>$-1.5$</td>
</tr>
<tr>
<td>LIW-LSW</td>
<td>$-2.9 \pm 1.6$</td>
<td>$-2.0$</td>
</tr>
</tbody>
</table>

The $O_2$/heat ratio for the LIW and LSW together is substantially smaller in magnitude, i.e., $-2.9 \pm 1.6$ nmol J$^{-1}$. Although the difference in the $O_2$/heat ratio between the two layers is not significant, the lower value at depth appears to be consistent with the findings of Keeling and Garcia (2002), who suggested a ratio of only about $-3$ nmol J$^{-1}$ for the waters associated with the formation of North Atlantic Deep Water. The $O_2$/heat ratios computed by depth yield similar values and depth trends, although with higher uncertainties (Table 3).

Comparing these ratios with those expected from solubility alone (about $-1.5$ nmol J$^{-1}$ for the upper density horizons and about $-2.0$ nmol J$^{-1}$ for the deeper horizons) reveal an enhancement factor of about three in the upper horizons and about 1.4 for the deeper horizons. Thus our upper ocean findings support the results of Keeling et al. (2010) who reported an enhancement factor of around four for thermocline waters. In contrast, Frölicher et al. (2009) found in their model study only an enhancement by a factor of two, more in line with our lower enhancement factor in the deeper density horizons. All in all, our oxygen loss to heat gain ratios support the long-standing hypothesis that ocean warming will lead to an over-proportional loss of oxygen. Our results are especially important because they demonstrate this behavior for the first time on the basis of long-term trends, which is especially important when these ratios are used for estimating past or future changes in the oceanic oxygen inventory (Keeling and Garcia, 2002; Keeling et al., 2010).

3.5 Summary and Conclusions

By building a high-quality oxygen data set for the North Atlantic, we have been able to estimate secular trends in dissolved oxygen over much longer periods and over much broader regions than hitherto possible. From our least-square linear trend analysis we found that the upper layers of the North Atlantic occupied by the UW, MW and IW lost on average about $-5.0 \pm 1.7 \mu$mol kg$^{-1}$ of oxygen between 1960 and 2009. This loss is not uniformly distributed but mostly concentrated in the eastern and northern North Atlantic. In contrast, the southwestern regions of the North Atlantic have actually gained oxygen. The contribution of the driving mechanisms also differs from region to region. The decrease of oxygen in the UW is driven by a warming induced reduction in solubility. The oxygen decreases observed in the northern and eastern part of the MW and IW is probably driven mainly by changes in circulation and ventilation, while the decrease observed in the central part of the North Atlantic in the IW is a combination of both circulation/remineralization and solubility changes.
with the solubility dominating. The increase of oxygen observed in the southwestern region is driven mainly by circulation changes. The trend analysis also shows an increase in the oxygen concentration in the domain of the LIW and LSW with an average oxygen gain of $5.5 \pm 2.6 \, \mu \text{mol kg}^{-1}$. The increase is rather uniformly distributed across all regions and is mainly driven by changes in solubility.

When integrating the oxygen changes across all horizons and regions, a statistically insignificant small net gain emerges. This hides, however, the fact that this small gain is actually the result of a near cancellation of a loss of $-58 \pm 20 \, \text{Tmol}$ in the upper layers and a gain of $70 \pm 34 \, \text{Tmol}$ in the deeper layers. Given the fact that the oxygen gain of the deeper layers is a result of a long-term trend of the NAO towards a more positive state, and that this trend has reversed sign since the mid-1990s, it is intriguing to speculate that the deeper layers of the North Atlantic likely will be losing oxygen in the coming decades. Some first indication of this reversal in the trend can be seen in the Labrador Sea, and likely will be spreading into the other regions in the coming years. The recent reversal of the NAO trend may also begin to reverse the trends in the upper density horizons in the coming decades. However, if global warming continues unabated, the resulting strong heating and the associated increase in stratification will likely overwhelm this effect, resulting in a possible future where the entire North Atlantic will be losing oxygen. Given our diagnosed strong scaling of the oxygen loss to heat gain of $-4.6 \pm 2.8 \, \text{nmol O}_2 \, \text{J}^{-1}$ for the upper density horizons (UW, MW, and IW) and $-2.9 \pm 1.6 \, \text{nmol O}_2 \, \text{J}^{-1}$ for the lower density horizons (LIW and LSW), any projected warming of the Atlantic ocean will make this loss substantial. Thus, our analysis strongly support the notion that if anthropogenic climate change continues to evolve unabated, the ocean is bound to deoxygenate with not well understood consequences for marine life. This is a source of concern, especially when considering that ocean deoxygenation is not occurring in isolation, but together with ocean acidification and ocean warming (Gruber, 2011).

Therefore, it is crucial to continue with the oxygen sampling in order to document the evolution of oxygen in the North Atlantic and to further improve the spatial and temporal coverage of the observations. For the time being, the only approach yielding oxygen data with sufficient accuracy is ship-based, but oxygen sensors on Argo float are continuously improving their performance, making the very valuable candidates for future monitoring of long-term oxygen trends.

### Acknowledgements

This work was supported by funds from ETH Zurich. We thank the numerous scientists and analysts responsible for the collection, and the analysis of the large amount of data that form the GLODAP, CARINA and WOD05 datasets. We also thank M. Rhein for sharing the data from the cruise MSM12/3. We are grateful to Toste Tanhua and the CARINA synthesis teams for their contributions and for sharing the many routines developed during this effort.
Chapter 4

Interannual to decadal oxygen variability in the Mode and Intermediate waters along 47°N in the eastern North Atlantic

I. Stendardo¹, N. Gruber¹, D. Kieke² and M. Rhein²

in preparation for *Deep Sea Research II (DSR-II)*

¹ Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Zürich, Switzerland

² Institute of Environmental Physics, Department Oceanography, University of Bremen, Bremen, Germany
Abstract

Analysis of a repeated hydrographic longitudinal section in the eastern North Atlantic at 47°N from 1993 to 2011, with almost yearly resolution until 2005, permitted us to investigate the interannual to decadal variability of the oxygen concentration in the Subpolar Mode Water (SPMW), Intermediate Water (IW) and Mediterranean Overflow Water (MOW). Our results show a consistent decrease in the oxygen concentration for all three water masses, with the largest changes occurring from 1993 to 2002, coincident with the northwestward shift of the Subpolar Front (SF) in the eastern North Atlantic. Due to the contraction of the SF in the earlier 2000s, SPMW in 1993 was replaced by SPMW of more southern origin in 2002, which is ventilated to lighter densities. The reduced ventilation of this water mass caused a decrease of oxygen concentration of $-1.8 \pm 0.7 \, \mu \text{mol kg}^{-1} \, \text{yr}^{-1}$. Also penetration of the IW into the SPMW contributes to the overall oxygen decrease in the SPMW. The contraction of the subpolar gyre moreover reduces the contribution of IW of subpolar origin into the region in favor of increased northward transport of IW of subtropical origin. The oxygen changes in this water mass is $-2.3 \pm 0.7 \, \mu \text{mol kg}^{-1} \, \text{yr}^{-1}$ from 1993 to 2002. Over the same period, the oxygen changes in the MOW are probably affected by the interplay between circulation and solubility changes. Less clear are the changes observed after 2002, which shows also decrease of oxygen but weaker and not significant due to the lack of data between 2006 and 2009. We also showed that mesoscale events in this region could be important, affecting the water column until at least 1000 m depth and for more than 300 km, inducing significant changes in the oxygen concentration.
4.1 Introduction

Ocean deoxygenation has gained increasing attention in the recent years, not only for its impact on the hypoxic regions of the ocean where further drops of $O_2$ concentrations would strongly affect marine ecosystems and elemental cycling (Stramma et al., 2008; Keeling et al., 2010), but also because of its sensitivity to climate change. Indeed several studies showed that global warming will cause a net loss of oxygen (Bopp et al., 2002; Plattner et al., 2002; Matear and Hirst, 2003), which is driven not only by the lowering solubility of the ocean due to warmer temperatures, but also because of increasing stratification that reduces the ventilation of water masses not directly in contact with the atmosphere (Keeling and Garcia, 2002; Matear and Hirst, 2003; Keeling et al., 2010). Observational analyses have revealed changes in the ocean over the last decades in most of ocean basins. For example changes in the oxygen concentrations were discussed for the North Atlantic in two studies from Johnson and Gruber (2007) and Stendardo and Gruber (2011). Negative changes in the oxygen concentration from 1988 to 2003 (Johnson and Gruber, 2007) and from 1960 to 2009 (Stendardo and Gruber, 2011) were found in the domain of mode and intermediate waters. Also in the Pacific Ocean, decreases in the oxygen content below the mixed layer until at least 1000 m depth were discussed for example in Emerson et al. (2004) and Whitney et al. (2007). All these changes were attributed to the interplay between the physical and biological mechanisms that are responsible for the distribution of the oxygen in the interior ocean. The individual contribution of these mechanisms however, is not yet entirely understood. Neither is it entirely clear whether these changes reflect natural fluctuations or are already the signal of anthropogenic climate changes.

Stendardo and Gruber (2011) for example showed negative trends in the $O_2$ concentration in the North Atlantic from 35°N to 60°N over the last 50 years, as a consequence of changes in solubility affecting mainly the upper part of the ocean, and changes in circulation and/or ventilation affecting mainly the mode and intermediate waters. Positive trends were found in the Lower Intermediate Water (LIW) and Labrador Sea Water (LSW) due to solubility changes. This study also revealed that superimposed on this long-term trend was a substantial amount of interannual to decadal variability that was not well resolved by the available data.

The aim of this study is to investigate the interannual to decadal $O_2$ changes in the North Atlantic. The study from Johnson and Gruber (2007) showed that in the subpolar North Atlantic Ocean, the oxygen concentration in the mode and intermediate waters has decreased over the last 20 years following a section at 20°W from Iceland to 40°N repeated four times in 1988, 1993, 1998 and 2003. The results from this study revealed that the main drivers for the observed oxygen changes were connected to circulation changes due to the NAO shift from strong positive to low positive values. However, Johnson and Gruber (2007) based their analysis on only four repeated transects spanning 20 years of observation, which prevents the analysis of the data on interannual time scale, thus making the attribution of the observed changes to decadal or interannual variability difficult. Thus, as been pointed out by Johnson and Gruber (2007), decadal sampling of a few sections may not be able to fully resolve the spatial and temporal distribution of the properties changes risking to aliasing changes that can be important for biogeochemical budgets. In this work we investigate the oxygen changes along a different repeated transects that crosses the Atlantic at about 47°N in the eastern North Atlantic from 30°W to 12°W, located to the south of the North Atlantic Current (NAC) northward branches in a
transient zone between the subpolar and the subtropical gyre with much higher temporal resolution. We use indeed a repeated transect in the eastern North Atlantic that was sampled from 1993 to 2011 with nearly annual resolution until 2005. Moreover, we aim to better understand the mechanisms involved in the oxygen changes in this region on interannual to decadal time scale considering that many studies has investigated the eastern North Atlantic in light of circulation changes, but few has related these changes to the observed oxygen changes. Indeed, some studies already investigated this particular line (Bersch, 2002; Bersch et al., 2007; Kieke et al., 2009), but while Kieke et al. (2009) focused only on the Upper Labrador Sea Water (ULSW) and LSW, Bersch (2002) and Bersch et al. (2007) focused on the LSW and a generic water layer above $\sigma_1 = 32.33$ kg m$^{-3}$, and none of the studies considered the changes in the oxygen concentration.

Subpolar Mode Water (SPMW), Intermediate Water (IW) and Mediterranean Overflow Water (MOW) are extremely important since they take part of the Meridional Overturning Circulation (MOC), SPMWs for example have an important role in the transfer of warm and salty North Atlantic water from the subtropical gyre to the Nordic Seas and Labrador Sea (Brambilla and Talley, 2008), the MOW is the high salinity signature of the North Atlantic Deep Water (NADW) (Talley et al., 2011). Moreover most of the oxygen changes seems to be concentrated in the domain of these water masses (Stendardo and Gruber, 2011), which makes them the best candidate to investigate the interannual and decadal oxygen variability.

### 4.2 Background

The repeated hydrography is on the eastern side of the North Atlantic between the Mid Atlantic Ridge and to the west of the Porcupine Bank (Fig. 4.1). Confined in the upper ocean and characterized by thick layers of low stability there is the SPMW (Talley, 1999). SPMW can be identified by a minimum in isopycnal potential vorticity (PV), corresponding to high vertical homogeneity of the water mass (Johnson and Gruber, 2007; Brambilla and Talley, 2008). There are usually different types of SPMWs that originate from the different branches of the NAC, and they are largely confined to the eastern North Atlantic (Brambilla and Talley, 2008), with their formation on the southeastern side of the NAC (shade area in figure 4.1). SPMW are highly oxygenated waters that reflect their well-ventilated nature. According to earlier studies (Talley, 1999), the SPMW are strongly connected to boundary regions and ridges, indeed intensification of the low PV were observed along all the boundary regions in the North Atlantic. In this region low PV is found at the eastern boundary. This also reflects in higher $O_2$ concentration along this boundary (Fig. 4.2a). Changes in the northern type of SPMW were identified along a section at 20°W and discussed by Johnson and Gruber (2007), where an increase in salinity, temperature and a decrease in density in 2003 compared to 1993 were described. The changes in that region were attributed to circulation changes resulting from the northwestward shift in the NAC that brought lighter, saltier and warmer SPMW at lighter density horizons. According to these authors this shift was attributed to the North Atlantic Oscillation (NAO).

Below the SPMW lays the IW, a layer of low-oxygen concentration and high PV. The IW found in this region represents a mixture of MOW advected northward (Reid, 1979), Antarctic Intermediate Water (AAIW) brought to the region by the NAC (Tsuchiya et al., 1992; Alvarez et al., 2004; Sarafanov
4.2. Background

Figure 4.1: Simplified circulation sketch of the upper and intermediate North Atlantic circulation superimposed on the North Atlantic Mean Dynamic Ocean Topography (1992-2002) (Maximenko et al., 2009). Contoured as black lines is the topography derived from the TerrainBase gridded at 5-minute intervals. Red and orange arrows shows the circulation pathway of the NAC, the shade area indicates the SPMW associated with the NAC based on (Brambilla and Talley, 2008); in green are the paths for the IW (Schmitz, 1996; Pollard et al., 2004) and in dark red the northward path of the MOW (Lozier and Stewart, 2008). The black lines represents the cruise track for the A2 and 47°N transects. The rectangle highlights the region of this study.

et al., 2008) and water originating in the subpolar western boundary current of the subpolar gyre (the Labrador Current), brought northeastward by the NAC (Pollard et al., 2004; Johnson and Gruber, 2007) and known as Subarctic Intermediate Water (SAIW). This path is represented by the green arrows in figure 4.1, based on Schmitz (1996) for the AAIW pathway, and as deduced from Pollard et al. (2004) for the SAIW pathway. The contribution of each of these waters to the overall IW is uncertain (Sarafanov et al., 2008). SAIW originates by mixing of warm saline water from the NAC with cold low-salinity water from the Labrador Current (Alvarez et al., 2004), and moves eastward following the NAC (Pollard et al., 2004). While the AAIW forms in the Southern Ocean and spread northward along the South Atlantic and is transported in the eastern North Atlantic by the Gulf Stream and then the NAC (Alvarez et al., 2004). Both water masses carry with them a signal of low oxygen due to combination of remineralization and circulation. This results in a horizontal oxygen distribution as inferred from the O2 climatology (Fig. 4.2), with medium-low oxygen concentration and without any evident east-west gradient in the eastern basin but rather a south-north gradient of high-low oxygen concentration. Changes in the IW in the eastern North Atlantic but at northern latitudes (53°N and
60°N) were described for example by (Sarafanov et al., 2008). They found an increase in salinity and temperature of the IW in the subpolar gyre from 1992 and 2002 at 53°N and from 1997 to 2005 at 60°N attributed to the increasing contribution of the source water masses (AAIW and MOW) extending northward.

Finally, another water mass clearly found in this region is the MOW. This warm and salty water mass flows out of the Mediterranean Sea through the Strait of Gibraltar and moves northward as a coherent mid-depth boundary current along the eastern coast of the North Atlantic. Similar to the IW, the MOW also brings a low-oxygen signal to the north, since this water mass moves along the eastern boundary its low-oxygen signal is stronger at the boundary, this translates into a low-east high-west oxygen horizontal distribution (Fig. 4.2). Its pathway is thought to continue along the Iberian Peninsula into the Bay of Biscay and onward toward the Porcupine Bank. Lozier and Stewart (2008) showed that the penetration of MOW into the northern North Atlantic depends on the spatial extent of the subpolar gyre into the northeastern basin. Indeed, they hypothesized that when the subpolar gyre contracts, the MOW is able to penetrate northward into the subpolar water, while this path it seems to be blocked when the subpolar gyre expands southeastward. Further studies seems to confirm this hypothesis (Bozec et al., 2011; Burkholder and Lozier, 2011). However, according to Burkholder and Lozier (2011) which based their study on a lagrangian approach, there is little evidence for a coherent poleward-flowing eastern boundary current, but rather an eastern North Atlantic flow field with strong

Figure 4.2: Climatological oxygen distributions at $\sigma_1 = 31.65$ a), $\sigma_1 = 31.80$ b) and $\sigma_1 = 32.10$ c) corresponding to the centers of SPMW, IW and MOW (from WOCE climatology (Gouretski and Koltermann, 2004)). In all the sketches the black lines show the location of transects in the eastern part of the North Atlantic.
temporal and spatial variability.

All these previous studies showed that distribution, pathway and properties of the water masses can change through years. Indeed, the North Atlantic subpolar circulation is subjected to substantial interannual to decadal changes, as suggested by several studies (Bersch, 2002; Bersch et al., 2007; Lozier and Stewart, 2008; Håkkinen and Rhines, 2009; Burkholder and Lozier, 2011). This has certainly an impact on the circulation of the upper waters involving the SPMW, IW and MOW. One of the main source of variability is the change in the position of the Subpolar Front (SF) associated with the strengthening or weakening of the subpolar gyre (Håkkinen and Rhines, 2004, 2009). The related salinity and temperature changes observed in the SPMW, IW and MOW resulted from the contraction of the subpolar gyre observed after the earlier 1990s, which causes a significant salinity and temperature increase in the subpolar North Atlantic (Håkkinen et al., 2011) due to a progressing penetration of water of subtropical origin into the northern regions. Finally, most of this variability was attributed to the NAO index shift towards strong positive values in the earlier 1990s to low positive (sometimes negative) in 2000s.

But how does the oxygen change in relation to these changes observed so far in the North Atlantic? Johnson and Gruber (2007); Stendardo and Gruber (2011) discussed that the oxygen concentration in the upper part of the water column shows high variability. Decreases of oxygen in the SPMW and IW due to reduced ventilation were observed in relation to the changes in the subpolar circulation from a different set of data with much lower temporal resolution (Johnson and Gruber, 2007). We have now the opportunity to analyze a time window that covers the earlier 1990s, characterized by strong subpolar gyre circulation, the 2000s characterized by the westward movement of the SF, until 2011 (the most recent year), with a fairly good resolution allowing us not only to investigate the decadal changes but also the interannual variability.

### 4.3 Methods

**Table 4.1:** Cruises information on hydrographic sections in the eastern North Atlantic.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Period</th>
<th>Research vessel</th>
<th>Line</th>
</tr>
</thead>
<tbody>
<tr>
<td>G226/2</td>
<td>July 1993</td>
<td>Gauss</td>
<td>A2</td>
</tr>
<tr>
<td>M30/2</td>
<td>Oct-Nov 1994</td>
<td>Meteor</td>
<td>A2</td>
</tr>
<tr>
<td>G276/2</td>
<td>May-Jun 1996</td>
<td>Gauss</td>
<td>A2</td>
</tr>
<tr>
<td>M39/3</td>
<td>Jun-Jul 1997</td>
<td>Meteor</td>
<td>A2</td>
</tr>
<tr>
<td>G316/1</td>
<td>Apr-May 1998</td>
<td>Gauss</td>
<td>A2</td>
</tr>
<tr>
<td>G350/1</td>
<td>May-Jun 2000</td>
<td>Gauss</td>
<td>A2</td>
</tr>
<tr>
<td>M50/4</td>
<td>Jul-Aug 2001</td>
<td>Meteor</td>
<td>A2 (only west of 30°W)</td>
</tr>
<tr>
<td>G384/1</td>
<td>May-Jun 2002</td>
<td>Gauss</td>
<td>A2</td>
</tr>
<tr>
<td>M59/2</td>
<td>Aug 2003</td>
<td>Meteor</td>
<td>47°N</td>
</tr>
<tr>
<td>Subpolar05</td>
<td>Jun 2005</td>
<td>Thalassa</td>
<td>47°N</td>
</tr>
<tr>
<td>M82/2</td>
<td>Aug-Sep 2010</td>
<td>Meteor</td>
<td>47°N</td>
</tr>
<tr>
<td>M85/1</td>
<td>Jul-Aug 2011</td>
<td>Meteor</td>
<td>47°N</td>
</tr>
</tbody>
</table>
We used data from two repeated hydrographic transects, the historical A2 WOCE section whose occupation started in 1993 until 2002 with almost yearly resolution, and the 47°N whose occupations continued in 2003 until 2011. The two lines are at different latitudes in the Newfoundland Basin (Fig. 4.1), with the 47°N occupying the northernmost region, but they merge in the eastern basin, allowing us to display all the cruises in one line in the Western European Basin. Unfortunately we lack of oxygen observations between 2006 and 2009. A summary of the cruises is listed in Table 4.1.

We used data from CTD (Conductivity, Temperature, and Depth) to compute temperature, salinity and density profiles that will be used to compare with oxygen profiles also taken from CTD. However, we used CTD oxygen data only for the cruises where the data were routinely calibrated against Winkler titration. This was the case for the majority of the cruises, except for M39/3 in 1997 where CTD oxygen was flag as questionable. For this cruise we used the bottle oxygen that has been linearly interpolated to 2-dbar pressure intervals, corresponding to the resolution of all CTD profiles. The accuracy of the oxygen measurements is thought to range between ±1 to ±3 µmol kg\(^{-1}\), depending from the cruises. The accuracies of temperature and salinity measurements were 0.002—0.003°C and 0.0020—0.0025 respectively (Kieke et al., 2009).

Some of the cruises (M30/2, G350/1 and M59/2) were included in CARINA dataset, which allows us to quality control the bottle data of our selected cruises against CARINA, since the bottle data were used for calibrating the CTD. We performed the cross-over analysis and compute the offsets between our cruises and CARINA based on Tanhua et al. (2010b). None of the cruises needed to be adjusted against CARINA.

We focus on the upper ocean from 100 m depth to 1500 m depth, therefore we calculated the potential density referenced to 1000 m depth (\(\sigma_1\)). We also computed the PV that can be expressed in terms of Brunt-Väisälä frequency (\(f/g\))\(N^2\). PV is an important parameter not only for recognizing the SPMW by its pronounced PV minimum, but also to detect changes in ventilation, since an increase in PV is associated with a decrease of ventilation. We also compute the apparent oxygen utilization (AOU) defined as \([O_2]_{\text{sat}} - [O_2]_{\text{observed}}\), with the saturation concentration \([O_2]_{\text{sat}}\) computed using the equation of Weiss (1970). AOU represents the remineralized component of oxygen after removing the surface water O\(_2\) signature represented by the \([O_2]_{\text{sat}}\) (Sarmiento and Gruber, 2006).

All the vertical profiles of \(\sigma_1\), \(\theta\), salinity, oxygen and AOU were filtered with a moving average filter of 20-dbar resolution, whereas PV was filtered with a moving average filter of 160-dbar resolution. The filtered data are then interpolated on a regular \(\sigma_1\) grid of 0.001 kg m\(^{-3}\) resolution using a Piecewise Cubic Hermite interpolation for the profile in isopycnal layers. For the profiles in pressure coordinates, used to compute the average sections in Fig. 4.3, the parameters and the pressure were first interpolated on a regular \(\sigma_1\) grid and then converted back to a regular pressure grid of 20 dbar resolution, similar to the approach used by Johnson and Gruber (2007). For the sections analysis each station was linearly interpolated horizontally on a regular grid with 0.5 degree longitude resolution. To exclude from our analysis the seasonal variability, we removed all data above 100 dbar, moreover since the analysis was mainly done on isopycnals, we removed all the isopycnals that outcrops in winter. This was done by comparing our isopycnals with the surface winter \(\sigma_1\) taken from the World Ocean Atlas (2009).
4.3.1 Water Mass Properties

To perform the analysis on water masses we need to identify the density ranges in which SPMW, IW and MOW are found on this transect. Following the definition from other studies (McCartney and Talley, 1982; Talley, 1999; Read, 2001; Brambilla and Talley, 2008) we identified the SPMW by a minimum of PV. From the PV mean section (Fig. 4.3c) we can observe a minimum in PV confined to the pressure range 200–600 dbar, at the eastern boundary the minimum can be at the magnitude of $8.7 \times 10^{-12}$ m$^{-1}$ s$^{-1}$. The PV shows an increase from east to west showing that SPMW is more at the boundary. This same east-west gradient is found also in oxygen concentration (Fig. 4.3b) that in these water masses can have values as high as 295 $\mu$mol kg$^{-1}$, in agreement with the oxygen distribution shown from the climatology in Fig. 4.2. The SPMW ranges between $\sigma_1$ of 31.55 and 31.75 kg m$^{-3}$. However, the choice of this density range excludes some of the SPMW that is found at lighter density at the western side from 30°W to 24°W, that are however too shallow, with the consequence that the density range we selected does not have SPMW west of 25°W. The salinity of this water mass is between 35.4 and 35.6 (Fig. 4.3a) and $\theta$ between 10–11.5°C. It also shows that the salinity is higher
in the eastern side compared to the western side of the section (Fig. 4.3a).

Following the criteria from Sarafanov et al. (2008), we identify the IW as a layer with an oxygen minimum of less than 230 $\mu$mol kg$^{-1}$. The $\sigma_1$ density range in which this oxygen minimum is embedded is $31.75 - 32.0$ kg m$^{-3}$ (Fig. 4.3b). However, at the eastern boundary the $O_2$ minimum is at higher density because of the penetration in this layer of the MOW, marked by a maximum in salinity close to the eastern boundary (Fig. 4.3a), ranging between $\sigma_1 = 31.90 - 32.20$ kg m$^{-3}$. To try to separate the two water masses we considered as IW density range $\sigma_1 = 31.75 - 31.90$ kg m$^{-3}$. This density range also shows a maximum in PV (Fig. 4.3c). Regarding the salinity concentration, we can identify the IW as a water mass with salinity lower than 35.3, centered at the oxygen minimum range with a temperature of about 5.5$-9.5^\circ$C. IW was detected as a vertical minimum of salinity $S<34.9$ and $\theta$ of around 6$-7^\circ$C by Pollard et al. (2004), and of salinity $S<35.1$ near the density $\sigma_1=32.15$ kg m$^{-3}$ at around 53$^\circ$N by Johnson and Gruber (2007). This section does not have IW as fresh as the one identified by Pollard et al. (2004), because of the mixing of this water mass with saltier water, like the MOW, and because of the location further south close to the water of southern origin. The pressure range of IW is about 500$-800$ dbar, shallower at the western side (500$-600$ dbar) compared to the eastern side (600$-800$ dbar).

As already mentioned, MOW is recognizable for the high salinity concentration at the eastern boundary in the density range $\sigma_1 = 31.9 - 32.2$ kg m$^{-3}$ (centered at $\sigma_1 = 32.1$ kg m$^{-3}$) at around 1000 dbar (Fig. 4.3a). Regarding the oxygen distribution, the MOW is still in the range of oxygen minimum but shows lower oxygen concentrations in the eastern boundary, while the oxygen increases westward and opposite to the longitudinal gradient observed in the SPMW, which is in agreement with the climatological $O_2$ distribution in Fig. 4.2. Moreover, in the density range of MOW can also penetrates water coming from the western side of the section, such as the ULSW. The LSW is a water mass that forms in the Labrador Sea as a result of strong winter deep convection. It has two types, a deeper one usually found on higher density ranges and a shallower one the ULSW, which is found at lighter density. Kieke et al. (2009) showed that the isopycnal chosen to identify the ULSW extended into the MOW in the eastern side of the Mid Atlantic Ridge (MAR). All these considerations makes clear that the MOW west of 15$^\circ$W is strongly diluted.

### 4.4 Results

We calculated the mean AOU distribution from the available section and computed the difference between each section and this mean (Fig. 4.4). The AOU distribution shows quite high interannual variability, although we can still distinguish some general patterns, as for example the fact that the earlier transects from 1993 to 1997 have mostly negative changes in the AOU in the domain of the SPMW, IW, while starting from 1998 the AOU changes to positive values, except the 2003 occupation, in which negative values prevail above the MAR at about 27$^\circ$W. In 1998 the increase in AOU is just limited between 30$^\circ$W to 25$^\circ$W, while it extends until 20$^\circ$W in 2000 and finally involves the entire longitudinal section in 2002. From 2005 and 2011 positive AOU also extends along the entire section, although there are also some negative values. Moreover, highlighted from the contour lines of the pressure, it is possible to distinguish some eddy features pronounced by strong doming of the isobars,
4.4. Results

`\(\sigma_1\)`—Longitude distribution for AOU (\(\mu\text{mol kg}^{-1}\)) displayed along the eastern part of 47\(^\circ\)N/A2 section for the period 1993–2011. AOU is displayed as the particular deviation from the mean AOU distribution derived from averaging all available sections. The sections are masked for the winter outcrop, computed with the winter surface \(\sigma_1\) from the WOA09 and represented by the black dashed line. Black contours lines denote pressure in dbar, pressure below 1500 dbar and less than 100 dbar are excluded.

In 1997, 2000, 2001, 2002 and 2003, that seems to impact the AOU distribution, mostly showing decrease in AOU in correspondence to the domes. These mesoscale events will be discussed later in the text. Finally, most of the spatial and temporal variability is located at pressure lower than 1000 dbar.

To follow the temporal and spatial evolution of the mode and intermediate waters we display longitudinal changes in the water properties through time as a Hovmöller diagram. Figures 4.5, 4.9 and 4.10 show the temporal evolution of oxygen, AOU, \(\theta\), salinity, PV and pressure in the SPMW, IW and MOW respectively.
4.4.1 SPMW Changes

Since the density range selected for the SPMW in this section does not have SPMW west of 25°W, we will consider only the changes east of this longitude. We first discuss oxygen changes in the SPMW (see Fig. 4.5a). Figures 4.5(a, d) show the oxygen gradient between the eastern and western parts of the transect, highlighted from the climatology in Fig. 4.1a. In this density range the oxygen (AOU) concentrations increase (decrease) from west to east. The SPMW found along this section probably originates from one of the southern branches of the NAC that moves toward the Rockall Trough after crossing the MAR. Moreover, the section is also located between the subpolar gyre normally characterized by higher O_2 concentration and the subtropical gyre that has on average lower O_2 concentrations. Figure 4.5a shows that the gradient from west to east is weakening throughout the years from 1993 to 2002, starting from 2005 the high O_2 concentration remains more or less confined to the eastern boundary. The year 2010 unfortunately lacks of data at the eastern boundary, but the year 2011 shows that the high O_2 concentration at the boundary is increasing. In 2003 the oxygen (AOU) increase (decrease), this sudden changes was however due to a meandering feature developed from eddies in that area at that time that will be describe in more detail in a separate section, these eddies were tracked on top of the MAR. Nevertheless, the oxygen also increases east of the MAR until 18°W and it is followed by an increase of the thickness of the layers (not shown) and decrease

**Figure 4.5:** Hovmöller diagram showing the time evolution of O_2 a), \(\theta\) b), PV c), AOU d), Salinity e) and pressure f), along 47°N for the SPMW. The density range for the SPMW is \(\sigma_1 = 31.55-31.75\ \text{kg m}^{-3}\). Shades show years with missing data. In the lower panels it is shown the topography and the \(\sigma_1\) density range on a pressure grid of SPMW. Please notice non linear color scale for O_2, AOU and PV.
in PV (Figure 4.5 c). Changes in PV are similar to the changes observed in the AOU and O$_2$, if we exclude the 1993 and 1994 where high PV values are observed at the eastern boundary between 28°W to 22°W.

By looking at the time evolution of the properties versus the isopycnal layers for different slices of the transect as shown in Fig. 4.6 and Fig. 4.7 we can deduce how these properties changes through time along the isopycnals. We observe in Fig. 4.6 (j−l) that the SPMW gets ventilated towards shallower isopycnals from 1993 to 2005, shown in the figure as a movement of the minimum in PV towards shallower isopycnals. This is an indication that SPMW in 2005 was ventilated at lighter densities compared to the SPMW in 1993, while the denser isopycnals, which in 1993 had low PV (strong ventilation), in 2005 had higher PV (weak ventilation). At the same time the isopycnals are deepening (Fig. 4.7j−l), which means that the same isopycnal in 1993 was at shallower depth compared to 2005. This is also highlighted from the pressure time series in Fig. 4.8f, where the pressure increases until 2002 while it apparently reverses afterwards.

![Figure 4.6: Time evolution of O$_2$ (μmol kg$^{-1}$) a−d, AOU (μmol kg$^{-1}$) e−h, and PV (10$^{-12}$ m$^{-1}$ s$^{-1}$) i−l, along isopycnals ($\sigma_1$). The black lines indicate the density ranges of SPMW, IW and MOW. Shaded rectangles indicate years with missing data.](image)

The temporal evolution of the parameters shown in Fig. 4.8 can help to have a better overview of the changes happening in the SPMW. In this figure highlighted again is the decrease (increase) of oxygen
(AOU) until at least 2002 and the sudden increase observed in 2003 and weaker changes from 2005 to 2011. In Fig. 4.8d the PV in 1993 and 1994 was extremely high compared to the following years revealing an extremely low ventilation in these two years of the lighter density ranges of the SPMW not present in none of the following years. This results in no correlation between the $O_2$ changes and PV changes ($r^2 = 0.02$), but high correlation is shown for the changes in $O_2$ compared to the changes in the layer thickness ($r^2 = 0.82$).

The deepening of the isopycnals from 1993 to 2002 indicates that in during this time there is a replacement of lighter water on top of the isopycnal layers that were usually ventilated in 1993 but that are not longer ventilated in 2002. The correlation coefficient between PV and pressure is only 0.31 but increases to 0.48 if we consider only the easternmost slice that however is still low.

The oxygen trend computed over the first nine years is $-1.8 \pm 0.7 \mu$mol kg$^{-1}$ yr$^{-1}$, while it is weaker afterwards ($-0.2 \pm 2.1 \mu$mol kg$^{-1}$ yr$^{-1}$). But we have to consider the relatively huge gap from 2006 until 2009 where there are no observation, this makes the calculation of the trend from 2003 to 2011 highly uncertain.
4.4. Results

Salinity and temperature (Fig. 4.5b and e) show a weak correlation with changes in oxygen and AOU ($r^2=0.16$ and 0.24 respectively). Instead the salinity (followed by the temperature since the analysis is done on isopycnal layers) varies between higher and lower values, with two main peaks in 1993 and 1997 (figure 4.8e) followed by a freshening afterwards.

4.4.2 IW Changes

From the time evolution of the oxygen along the longitudes in the Hovmöller diagram in Fig. 4.9a, we can observe two major results, first of all there is a decrease of oxygen from 1993 to 2011, second, there is a difference between the western and the eastern side of the transect over the years. In Fig. 4.9a we indeed observe an oxygen gradient that goes from higher to lower oxygen from east to west, which

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**Figure 4.8:** Trends for oxygen, layer thickness, AOU, PV, salinity and pressure for the SPMW (in red) (from 25°W to 12°W), IW (in blue) (from 30°W to 12°W) and MOW (in black) (from 30°W to 12°W). Gray shades highlights years with missing data.
is different from what was expected based from the climatology that did not indicate any particular gradient between east and west. In 1993 higher O$_2$ concentrations are observed almost throughout the entire domain, except for the western side from 30°W to 28°W where the O$_2$ are lower. From 1993 to 2001 the oxygen decreased and the gradient weakens. After 2001 the O$_2$ concentrations remain low along the entire transect, although it is still possible to observe a decrease in the O$_2$ concentration, whose decrease is more evident in the O$_2$ trend in Fig. 4.8a. In 2003 the same sudden increase in oxygen observed in the SPMW is also present in the IW, showing that mesoscale events can affect great portions of the water column. The AOU and the PV show also similar pattern (Fig. 4.9c, d). Changes in PV and layer thickness show high correlation with the changes in O$_2$ (for both the $r^2 = 0.88$). The presence of an oxygen east-west gradient suggests that in 1993 the IW was characterized by water of subpolar origin that had higher oxygen concentration at the eastern boundary, while in 2002 this water was replaced by water of subtropical origin which includes also an increase in the input of MOW. The IW shows a similar oxygen trend as the SPMW (figure 4.8a). For the first nine years, from 1993 to 2002, it is equal to $-2.3 \pm 0.7 \mu$mol kg$^{-1}$ yr$^{-1}$, from 2003 to 2011 the annual rate of change in oxygen is weaker ($-0.5 \pm 1.4 \mu$mol kg$^{-1}$ yr$^{-1}$) and highly uncertain due to the lack of data from 2006 to 2009.

Regarding the salinity and the temperature changes, there is no strong correlation between the changes observed in oxygen and salinity or temperature changes (Fig. 4.9b, e). However, we find that the

![Figure 4.9](image-url)  
**Figure 4.9:** Hovmöller diagram showing the time evolution of O$_2$ a), θ b), PV c), AOU d), Salinity e) and pressure f), along 47°N for the IW. The density range for the IW is $\sigma_1 = 31.75-31.9$ kg m$^{-3}$. Shades show years with missing data. In the lower panels it is shown the topography and the $\sigma_1$ density range on a pressure grid of IW. Please notice non linear color scale for O$_2$, AOU and PV.
4.4. Results

Salinity increases between 1993 and 2001 despite some interannual variability (Fig. 4.8e). After 2001 a decrease in salinity is found (accompanied by a decrease in temperature) which is not compensated since we observe a similar oscillation in the pressure, implying a deepening of the isopycnal until 2001 and a shoaling of the isopycnal afterward (Fig. 4.9f). This is supported by looking at the mean trends in Fig. 4.8f. The PV maximum is expanding and moving towards lighter densities from the beginning of the observations to the end (Fig. 4.6c).

4.4.3 MOW Changes

Fig. 4.10: Hovmöller diagram showing the time evolution of O$_2$ a), θ b), PV c), AOU d), Salinity e) and pressure f), along the longitude for the MOW. The density range for the MOW is $\sigma_1 = 31.9$-$32.2$ kg m$^{-3}$. Shades show years with missing data. In the lower panels it is shown the topography and the $\sigma_1$ density range on a pressure grid of MOW. Please notice the non linear color scale for O$_2$, AOU and PV.

Fig. 4.10a shows that the oxygen concentrations are usually lower on the eastern side than on the western side, as expected from the climatological O$_2$ distribution. We can expect that the lower oxygen concentration at the boundary are a signature of MOW since the source of this water mass is located closer to the eastern boundary than to the western side of the section. Thus, from Fig. 4.10 (a, e), oxygen changes similar to salinity from higher values in 1993 to lower values in 2002 and then again back to higher values, as also shown in Fig. 4.8 (a, e). The similarity to salinity (shown in Fig. 4.10e) is also represented by the high correlation between the changes of the two properties ($R^2 = 0.72$). Fig. 4.10a also shows that the low oxygen signature of MOW at the eastern boundary (lower than 204 µmol kg$^{-1}$) intensified from 1993 to 2002 progressively toward the west, in 2003 this signal weakens...
and afterward it remains confined between 18°W and 21°W. Moreover, from Fig. 4.7d it is possible to observe a pulse of high salinity at the eastern boundary in 1998 and 2002 that extends until 20°W, this high salinity seems also to impact the oxygen distribution as revealed by the expansion of the O$_2$ minimum (Fig. 4.10a and Fig. 4.6d).

The O$_2$ trend computed from 1993 to 2002 is $-1.1 \pm 0.5 \mu$mol kg$^{-1}$ yr$^{-1}$, and $0.08 \pm 0.76 \mu$mol kg$^{-1}$ yr$^{-1}$ from 2003 to 2011. The AOU distribution strongly differs from the O$_2$ distribution (Fig. 4.10d), indeed the AOU pattern resembles more the pattern we observed for the SPMW and IW, with an increase in the AOU that progressively strengthen toward the east until 2002. From 2003 to 2011 the changes are extremely weak.

The difference between the O$_2$ and AOU distributions might be an indication that the changes in O$_2$ concentration in the MOW are the result of solubility changes due to the changes in salinity and temperature. The distribution of the O$_2$ in the Høvsmoller diagram resemble the salinity distribution, while the AOU distribution resemble the PV distribution. The correlation between AOU and salinity is only 0.39, lower that the correlation between O$_2$ and salinity. However, the correlation between AOU and PV is even lower ($r^2 = 0.30$). This might depend from the fact that the changes in AOU are relatively weak and this might affect the correlation.

### 4.4.4 Eddy events in 2003

Of particular interest is a feature that appears on the 20$^{th}$ of August 2003. Fig. 4.4i, which corresponds to the section difference between the AOU in 2003 and the climatology, shows a prominent decrease in AOU between 30°W and 25°W over the MAR. Fig.4.4i also denotes a strong doming of the isobars over the MAR that goes in line with the strong negative AOU compared to the mean distribution and that stretches over the density range $\sigma_1 = 31.5-32$ kg m$^{-3}$. Moreover, it has a lateral extension of about 379 km. This doming shape of the pressure contours points toward the presence of mesoscale eddies. In the ocean we can distinguish among three kind of eddies, a cyclonic eddy that has a negative signature of the sea level anomaly and a doming of the isopycnals on pressure coordinates, an anticyclonic eddy that has a positive signature of the sea level anomaly and a depression of the isopycnals on pressure coordinates, and a mode-water eddy that derives its name from the presence of a thick lens of water that deepens the isopycnals of the main pycnocline while doming the isopycnal of the seasonal pycnocline. Like the anticyclonic eddy, the mode-water eddy has a positive signature of the sea level anomaly since the depression of the isopycnals of the main pycnocline dominates on the geostrophic velocities (McGillicuddy et al., 2007).

Our hypothesis is that the changes in AOU in 2003 are a result from mesoscale eddies forming in that location at that time, which might be the primary driving force for the observed changes. From the altimeter data available from Archiving, Validation, and Interpretation of Satellite Oceanographic Data (AVISO), we used the updated version of the Maps of Absolute Dynamic Topography (MADT), 1/3° spatial resolution and one week resolution centered at the day when the eddies were observed, the 20$^{th}$ of August 2003 (Fig. 4.11a). From this map it is possible to infer the presence of several eddies and filaments in the area where the cruise track crosses the MAR. In particular there are two stations that caught two eddies, these are the stations where we observed the strong AOU decrease (marked on the map with open white circles). One of the eddies is characterized by a regional minimum in
the absolute dynamic topography and therefore can be classified as a cyclonic eddy. The second one found more on the east is characterized by regional maximum in the absolute dynamic topography. Both the anticyclonic and the mode-water eddies can have regional maximum in the absolute dynamic topography. The difference between the two can be inferred from the impact they have in the water column. This is shown in Fig. 4.11 (b-e) where oxygen, salinity and temperature are represented along the pressure-longitude sections. According to the definition from McGillicuddy et al. (2007), the eastern station (highlighted with red triangles in Fig. 4.11 b-e) caught a mode-water eddy rather
than an anticyclonic eddy. This is revealed by the fact that we observe a deepening of the isopycnal below 500 dbar and a doming of the isopycnals above. The lens of water traps in this mode-water eddy is characterized by a well mixed layer of water with high oxygen embedded between more stratified layers as revealed from the vertical profiles (Fig. 4.11 f-h). Low PV (not shown) indicates that this water lens exhibited strong ventilation event, suggesting that the water masses characterizing the eddy core were formed during a deep winter mixing event and are more recent than the surrounding waters (Reverdin et al., 2009). Similar eddies were found in this area by Reverdin et al. (2009). These authors described a similar eddy with same characteristics ($T = 11-12^\circ C$ and $S = 35.5-35.6$). They showed that these eddies can have a very long life in the eastern Atlantic, and can persist for more than three years. The impact of the cyclonic and the mode-water eddies on the AOU distribution is on the same direction, both eddies indeed cause a decrease of AOU (on average $-36 \mu$mol kg$^{-1}$ compared to the mean distribution) in the water column until at least 700 dbar well into the domain of IW and MOW. Regarding the cyclonic eddy, the AOU decreases because water of subpolar origin is brought there from the cyclonic eddy. This water is characterized by higher $O_2$ concentration and has lower salinity and temperature (Fig. 4.11f-h) compared to the IW and MOW found in this region. Regarding the mode-water eddy, according to Reverdin et al. (2009), the water properties point out to an origin of the mode-water eddy, found in their study, from the Bay of Biscay area. The eddy found in this study has similar characteristic, this point out that also this eddy might be formed in that area. In the Bay of Biscay a water mass called Eastern North Central Water (ENACW) forms during winter mixing and it is bounded between the NAC and the Azores Current (AC) (Gonzalez-Pola et al., 2005). The ENACW has similar water properties (salinity and temperature) of those of the mode-water eddy found in 2003. This can be an indication that the mode-water eddy found in 2003 could be formed as well in the Bay of Biscay.

In Fig. 4.4 we have noticed other similar features in 1997, 2000, 2001 all between 15$^\circ$W and 20$^\circ$W with a similar structure as the mode-water eddy observed in 2003. Although of weaker entity compared to the 2003, these eddies are responsible for the observed decrease in AOU in that region. In 2000 between 25$^\circ$W and 30$^\circ$W there is a doming of the pressure that recall an anticyclonic eddy structure, this can be the main driven mechanisms for the increase in AOU in the first 600 m depth until $\sigma_1 = 31.8$ kg m$^{-3}$. Anticyclonic eddies can be indeed responsible to bring water of subtropical origin trap in their core. The 2003 event was however exceptional since two different type of eddies with the same effect on the AOU were found close to each other causing the strong decrease in AOU observed in that particular year.

### 4.5 Discussion

The analysis of a repeated hydrographic transect at 47$^\circ$N in the eastern North Atlantic allowed us to investigate interannual and decadal changes in the oxygen concentration in the upper 1500 m of the water column.

The NAC crosses the Atlantic Ocean in a northeast direction consisting of two to four narrow branches that meander across the Atlantic in the latitude band 45$^\circ$N–53$^\circ$N (Bower and Von Appen, 2008). According to these authors, the northern branch of the NAC which is known as Subpolar Front (SF),
4.5. Discussion

exhibits high interannual variability while it crosses the MAR. Several studies have discussed the interannual to decadal changes in the pathway of the NAC in relation to the changes in the wind-stress pattern (Häkkinen and Rhines, 2004, 2009). Of particular interest for this study are changes in the spatial extension of the subpolar gyre in the eastern North Atlantic (Bersch, 2002; Bersch et al., 2007; Häkkinen and Rhines, 2004, 2009). According to these studies a contraction of the subpolar gyre was observed after 1995 associated with the weakening of the gyre circulation, due to the shift of the NAO index from strong positive values to low positive values. According to Bersch (2002) and Bersch et al. (2007) this contraction of the gyre caused a westward shift of the southeastern extension of the subpolar gyre in the Western European Basin in the upper layers, and a northward advection of saline subtropical water in its eastern part. This northward advection is balanced by the enhanced southward advection of subarctic waters west of the MAR from 1993 to 2002 do to the southeastward shift of the SF in the Newfoundland Basin. Häkkinen and Rhines (2009) confirmed these findings by showing that after 2001 a new path was open from the western subtropics to the subpolar latitudes as a consequence of the westward movement of subpolar gyre from 1992 to 2001 in the eastern North Atlantic. This shift allowed an expansion of subtropical more saline water northward. However a recent study from Häkkinen et al. (2011) shows that the NAO oscillation fails to predict the saline event after 2001. Häkkinen et al. (2011) found that the second EOF mode of the wind-stress curl represents better the gyre strength than the NAO index, since it readily projects on the Atlantic Ocean gyre by modulating the wind-stress curl which is responsible to form the gyres. This wind-stress curl second mode (second Principal Component PC2) seems to have many features in common with the NAO but appear to be separated from it. Moreover, the PC2 seems to vary with a period of 15 years with the most recent shift coincident with the NAO shift from strong positive in 1990s to low positive values 2000s.

How do these circulation changes affect the oxygen distribution in the SPMW, IW and MOW? According to our results the deepening of the SPMW isopycnals from 1993 to 2002 and the shoaling of PV minimum toward lighter densities, is an indication that the SPMW was replaced by lighter water on top of its layer. As a consequence the SPMW in 2002 is not longer ventilated at that densities causing a decrease in the O$_2$ concentrations. Shallower isopycnals are the signature of strong subpolar gyre circulation (like the one in 1993), while deeper isopycnals are signature of weak gyre circulation (like the one in 2002) Johnson and Gruber (2007). We did not find correlation between O$_2$ and PV which is attributed to the fact that in 1993 and 1994 extremely high PV values were found on top of the PV minimum, that was instead shifted toward higher densities. Consequently the high PV values penetrated into the density range of the SPMW. However, strong correlation between O$_2$ and layer thickness confirms that the decrease in the O$_2$ concentration in the SPMW can be attributed to decrease in ventilation, since the layer thickness is inversely correlated to PV. Therefore, the decrease in ventilation is attributed to the replacement of lighter, warmer and saltier water on top of SPMW that in 1993 was denser colder and fresher. The analysis reveals that at the beginning of the observations the SPMW was ventilated at greater densities, indicating that the SPMW was formed by a northern branch of the NAC, which produces colder and denser and more oxygenated water masses. This is in agreement with the fact that in 1993, well into the strong positive NAO phase and positive wind-stress curls (PC2), the gyre was expanded and the SF was at its southernmost extension. After 1995 the NAO index dropped to negative and afterward low positive phases and the wind-stress curl PC2 as well. This
has reduced the extension of the subpolar gyre to the north and shifted the SF to the west, as a consequence more SPMW of southern origin replaced the SPMW found in 1993, which is less oxygenated. Warmer SPMW can form for example from the southernmost branch of the NAC that after crossing the MAR diverts southward entering the subtropical gyre. Or ENACW forms in the Bay of Biscay can be advected to the region as a consequence of this entrainment of subtropical water toward the north. As a consequence for this entrainment we should observe a corresponding increase in salinity and temperature. An increase in salinity from 1993 to 2002 is observed in the IW and MOW domain but not clearly revealed in the SPMW. However if the SPMW moves to lighter densities, the density layers below can eventually be fed by a different type of water masses. The NAC while crossing the MAR carries on the same time more IW of subtropical origin into the region that is relatively fresher, colder and with low oxygen concentration compared to the SPMW on top but it is relatively warmer, saltier and less oxygenated compared to the IW of subpolar origin forming from the Labrador Current. The IW of subtropical origin could penetrates into the SPMW layer and masks the increase in salinity and induces the observed decrease of oxygen. Thus the weakening of the east-west gradient of oxygen observed in the figure 4.5a from 1993 to 2002 can be seen as a consequence of the west penetration of IW into the SPMW layer replacing the highly oxygenated SPMW with lower oxygenated IW. Our results also show that after 2002 the $O_2$ in the SPMW slightly decreases, but the changes are much weaker than the changes observed in the previous 9 years, however lack of data makes the calculation of this trend highly uncertain. Changes in the oxygen concentrations in SPMW might be also driven by local variations in buoyancy forcing, since formation of SPMW is directly linked to interaction with the atmosphere, so a decrease in the winter convection that forms the SPMW may also cause a decrease in the oxygen concentration or vice versa. However the NAO shift from positive to negative values should increase the winter ventilation in the eastern North Atlantic. We cannot verify the last hypothesis, however since the IW shows similar changes in the oxygen concentration, changes in the circulation due to the penetration of IW into the SPMW layer can better explain the observed changes. Unfortunately the interpretation of the results becomes difficult for the period from 2005 to 2011 due to the gap between the years. It seems that the entrainment of subtropical water reduced in 2005 but in 2011 there was a new pulse of high salinity water at the eastern boundary, but also lower PV and higher oxygen.

The oxygen changes in the IW can be also explained by circulation changes. The IW in this region is a mixture of SAIW from the subpolar gyre and of AAIW and MOW from the subtropical gyre. The first one represents the colder and fresher signature with relatively higher $O_2$ concentrations, and the last two represent the warmer and saltier signatures with lower oxygen. As observed for the SPMW, also the IW shows strong decrease of oxygen from 1993 to 2002, accompanied by increase in PV, and deepening of the isopycnals. The oxygen and PV changes are highly correlated. From Fig. 4.9a in the first period of the observation from 1993 to 2001 we highlighted an east-high west-low gradient of oxygen. This gradient can be a signature of water of subarctic origin, which is relatively more oxygenated compared to the IW of subtropical origin. After 2001 the gradient disappeared. With some variability the salinity increases until 2002, this confirms a decreasing influence of the SAIW toward an increasing influence of AAIW and MOW from the subtropical gyre. After a sudden increase in 2003, the oxygen lowers again, and this cannot be explained with the observed changes in salinity that instead decreases. We do not have enough information to understand this latter change in oxygen.
4.5. Discussion

Due to the depth structure of the observed changes Johnson and Gruber (2007); Stendardo and Gruber (2011), it is unlikely that the changes observed results from remineralization changes, although we cannot completely exclude this process, since we do not have observations to separate the biological effect from the circulation. Moreover, it is also possible that after 2002 there is an increase of the SAIW in the region, this however should be followed by an increase in oxygen, which is not observed. It is also possible that the contribution of AAIW has increased in the region compared to the MOW. The AAIW is fresher than the MOW and has lower oxygen. If this is the case we should observe an increase of westward transport of subtropical water into the region along the NAC pathway. Häkkinen and Rhines (2009) found an increase in the Eddy Kinetic Energy (EKE) east of the MAR at the fractures zones where the NAC is crossing the Ridge during 1999 and 2000. Bower and Von Appen (2008) showed that this EKE has stayed elevated at least until 2005. This might have increased the transport of AAIW into the region.

The oxygen decrease observed from 1993 to 2002 in the MOW can also be attributed to the same mechanisms described for the IW water. Salinity, pressure, PV and layer thickness changes indeed are similar to the changes observed in the IW and they have the same effect on the oxygen concentration. However, surprisingly the oxygen changes in the MOW differs from the changes observed in the IW after 2002, this is particularly evident in the 4.10. After 2002 the oxygen is slightly increasing following the observed decrease in salinity. We found high correlation between changes in oxygen and salinity that can be interpreted as changes in the oxygen induced by solubility changes. Kieke et al. (2009) identified the ULSW in a density range close to the range used in this study for the MOW, and an ULSW pulse arriving east of the MAR after 2001. The ULSW signal was unfortunately not clear east of 25°W due to mixing with eastern water with higher salinity, but the mixing with this fresher type of water with the MOW can explain the observed decrease of salinity after 2002 and this can also explain the observed oxygen increase. However these changes should also reflect into changes in AOU. This is not shown in the results. It can be probably hypothesized that the oxygen changes in the O₂ concentrations are driven by a combining effect of solubility and circulation changes due to mixing with more oxygenated water.

The MOW it has been often considered as a boundary current, indeed from the salinity section it was clearly shown a high salinity tongue at the eastern boundary that marked the MOW east of 15°W. However, this water masses has been already mixed along its northward spreading pathway. A recent study Burkholder and Lozier (2011) shows indeed little indication of a coherent eastern boundary current. They rather think that the northward progression of the MOW should be considered as a flow field, that only in the aggregate, forms a slow northward pathway. Thus it is not trivial to separate what is clearly a signal coming from the IW and from the MOW.

Finally, some of the changes can be driven by mesoscale event that in some particular case can be of strong impact, such as the feature described in 2003. This event protracted until the density range occupied by the MOW, thus until 1000 m depth. Other eddies were found in 1997, 2000 and 2001, that can be responsible for local increase in the oxygen. The event in 2003 remains however special since it shows two eddy features both, for different reasons, driving increase in the oxygen concentration in 2003. When considering interannual variability in the eastern North Atlantic, it is then important to take into account also these mesoscale events. This region is particularly interested by these event since the NAC pathway from west to east is characterized by high degree of eddy motion from west to...
east of the MAR (Bower and Von Appen, 2008), especially there is a tendency for the NAC to break up into a discrete number of eddies in the eastern basin after it crosses the MAR.

4.6 Conclusions

Observations from an hydrographic repeated section from 1993 and 2011 along 47°N in the eastern North Atlantic with almost yearly resolution until 2005, show that the oxygen concentrations in the SPMW, IW and MOW have undergone strong interannual variability showing a tendency for decadal ocean deoxygenation.

There is strong evidence that the decrease in the oxygen concentration from 1993 to 2002 in these water masses were mainly driven by changes in the ocean circulation. At the time of the observation, circulation in the eastern North Atlantic was affected by strong variability linked to the shift of the SF from east to west. This allowed water of subtropical origin to replace the SPMW of subpolar origin and reduces the ventilation of this water mass. At the same time at higher densities, in the domain of IW, SAIW was replaced also by water of subtropical origin formed by the MOW and AAIW that have relatively lower O\textsubscript{2} concentrations compared to the SAIW. Several studies investigated the eastern North Atlantic in relation to changes in circulation Bersch (2002); Häkkinen and Rhines (2004); Bersch et al. (2007); Johnson and Gruber (2007); Lozier and Stewart (2008); Sarafanov et al. (2008); Häkkinen and Rhines (2009) and spreading of saline signal toward the north. In particular Bersch (2002); Bersch et al. (2007) used a similar set of data from 1993 to 2002 (they did not have the cruise in 2001) to analyze the changes in the upper water circulation but without showing any oxygen changes. The conclusion from Bersch (2002); Bersch et al. (2007) fit into the observed oxygen decrease from 1993 to 2002, i.e. during periods with weak westerlies the eastward transport of subarctic waters with the NAC is reduced and the northward contribution of subtropical water enhanced. The consequences for the oxygen is that a reduced contribution of SAIW toward an increase contribution of AAIW and MOW, reduce the oxygen concentration in the IW layer in the eastern North Atlantic, since these two water masses have lower oxygen concentration. On the same time SPMW that was formed in 1993 from a northern branch of the NAC was replaced in 2002 by SPMW from a southern branch which is less ventilated, while at greater densities the AAIW and MOW penetrated into the SPMW reducing the oxygen. We do not have strong evidence that can explain how the contribution of AAIW and MOW changes through time due to the mixing of these two water masses that share similar densities. Moreover we could not exclude a mixing of ULSW entering the eastern North Atlantic in 2001 (Kieke et al., 2009). Since the gap between 2006 and 2009 it is not clear if the decrease in salinity observed after 2002 is caused by a reverse trend with increasing of subpolar water in the eastern North Atlantic, or reduction of the penetration of MOW, or increasing influence of AAIW over the MOW in the domain of the IW. We argued that the contributions of AAIW and MOW might have changed throughout the period of the observations, less MOW toward more AAIW could bring relatively fresher water but with less O\textsubscript{2} in the region after 2002. We also found that the oxygen changes in the MOW were also driven by changes in the solubility reflected in the high correlation between the oxygen and the salinity.

Many of the studies done on this area had related the circulation changes to NAO oscillation. Never-
4.6. Conclusions

Nevertheless, the NAO can not explain all the changes observed in this area, indeed we can not completely relates the changes observed in the region after 2002, although these are relatively weaker than the changes observe in the first period. According to Häkkinen et al. (2011) the NAO index is not always adequate to describe the ocean response to the atmospheric variability. They find that the second EOF mode of the wind stress curl is better to describe the response of the gyre circulation to changes of the wind-stress curl.

Moreover we also need to keep in mind that although the high temporal resolution of this this analysis, we are limited to the area and the data available for this region. To better understand the relationship with changes in the oxygen and contribution of the water masses to these changes other sources of data are needed that are independent from the set of data provided by the hydrographic section. This can help to understand better the individual contribution of the water masses in the region. For example by using altimeter data and Argo floats to track the changes back to their origin.

We found that some of the interannual changes were driven by mesoscale events that can extend their influence at least until 1000 m depth and for about 379 km. These events need to be taken into consideration when the goal is to investigate interannual variability, and when there are only a limit number of observations. Indeed, if the goal is to detect interannual to decadal changes these events can risk in biasing the results.

Finally in a previous study (Stendardo and Gruber, 2011) based on long-term changes in the oxygen concentration in the North Atlantic from 1960 to 2009, one of the main results was that the mode and intermediate water in the eastern North Atlantic lost oxygen over the last 49 years. The significant decrease in the oxygen observed in these water masses was related to reduction in ventilation and circulation due to the positive trend observed in the NAO after 1960s until 1990s with an emphasis on the reduction of ventilation due to buoyancy forcing in the mode water domain. In line with Johnson and Gruber (2007) we emphasized the role of the circulation on the oxygen changes, however unlike Johnson and Gruber (2007) we think that in light of the recent study from Häkkinen et al. (2011) these changes are related more to the wind-stress curl rather than to NAO shift. But further investigations need to be done to confirm this hypothesis. This raises the question on how might these two mechanisms, ventilation and circulation, interplay in determining the observed oxygen changes? Further analysis are need in order to answer to this question, and extremely important is to continue monitoring the oxygen variability into the ocean to further improve our understanding on the mechanisms driving these changes.

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Chapter 5

Summary and Outlook
The work done to perform a secondary quality control of previously unpublished hydrographic data, including oxygen measurements, in the North Atlantic, resulted in a high quality and internally consistent dataset named CARINA. The final product has data from 98 cruises (81 cruises containing oxygen observations) with a total of 103,414 bottle oxygen samples from 9,491 stations covering the period from 1977 to 2005. The secondary quality control used an inverse procedure based on a least square method that computes a set of adjustments to minimize the offsets among cruises with a minimum amount of adjustment. The data from the different cruises were compared in the deep ocean at cross-over locations to estimate the offsets. The adjustments were applied to 23 cruises out of 98. Most of the adjustments were between $\pm 1\%$ and $\pm 2\%$, with only five cruises needing adjustments higher than $2\%$. It was of fundamental importance for this PhD project to have this dataset ready for use. This gave me the opportunity to use CARINA to select more cruises from the WOD05. The selection procedure was based on the same criteria used to estimate the corrections in the CARINA dataset, i.e. I computed the offsets between CARINA and WOD05 cruises using the same routines developed from Tanhua et al. (2010b). However, I did not apply any corrections to the WOD05 cruises, but I selected only the cruises that did not require any major correction. Only cruises that required an adjustment of less than $1\%$ were selected. This solution resulted in a tremendous reduction of the available cruises from the WOD05: from a total of 5,645 cruises spanning from 1960 to 2004, only 184 cruises spanning the period from 1960 to 2000 met my requirements. Since some GLODAP cruises were used as core cruises (high quality cruises used as reference cruises) for the secondary quality control of CARINA, the two datasets could be easily combined. Thus, the final dataset used for the long-term trend analysis combines CARINA, GLODAP and WOD05 and contains 331 cruises, 22,849 stations and a total of 465,998 observations from 1960 to 2005, augmented with one unpublished cruise in 2009 (MSM12/3). The quality of the data has to be the primary goal for analyses whose focus is on temporal changes in some properties, since errors in the data can badly compromise the results. For example, in a work from Garcia et al. (1998) 30% of the observed changes in oxygen concentration were attributed to measurement errors. It was therefore of fundamental importance for my analysis to have a dataset internally consistent. However, to repeat the same kind of secondary quality control on WOD05 would involve an enormous amount of work due to the larger number of cruises in the WOD05 compared to the CARINA dataset. This was beyond the goal of this thesis, but it came with the penalty to have substantially less data available. Given the increased interest of the scientific community in oxygen-related issues, it would be a good opportunity to assemble a dataset built around oxygen-related parameters, as much CARINA was built around carbon-related parameters. This would be a valuable tool not only to continue to investigate long-term changes in oxygen but also to validate and calibrate the ARGO-O$_2$ floats that are deployed in the ocean.

The resulting dataset was used to investigate the oxygen trends in the North Atlantic for the last five decades. The analysis was performed on isopycnal density layers encompassing particular water masses. The North Atlantic was divided into eight regions based on topography and circulation patterns. The results from this analysis show that on average the UW, MW and IW lost $-5.1 \pm 1.7 \mu\text{mol kg}^{-1}$ of oxygen in the last 49 years. However, this decrease is not uniformly distributed, but is concentrated in the eastern North Atlantic. In an attempt to attribute processes to the observed changes I computed the changes in oxygen concentration in terms of $-\text{AOU}$, $O_2\text{sat}$ and $O_2^*$ in order to separate the effect of remineralization/circulation, solubility and gas-exchange. This exercise tells
us that the main driver for the UW ocean deoxygenation is solubility. Ventilation and circulation are the main drivers for the decrease observed in the northern and eastern part of the MW and IW. The combination of these two factors and solubility are driving the decrease in oxygen in the central region of the IW, with the solubility dominating. The increase in the oxygen observed in the western part is driven mainly by circulation changes. Regarding the deeper water masses, LIW and LSW, the analysis revealed that on average the oxygen concentration has increased from 1960 to 2009 by $5.5 \pm 2.6 \mu\text{mol kg}^{-1}$. This increase is attributed mainly to the solubility effect. For this last result, however, the trend analysis shows that due to warming of LSW starting after the early 1990s, the oxygen trend has reversed. Finally, given a loss of $-58 \pm 20$ Tmol in the upper layers (UW, MW and IW), and a gain of $70 \pm 34$ Tmol in the deeper layers (LIW and LIW) I estimated the $O_2$ loss to heat gain ratio to be $-4.6 \pm 2.8$ nmol J$^{-1}$ in the upper layers, about three times higher than the expected ratio from solubility alone, and $-2.9 \pm 1.9$ nmol J$^{-1}$ for the deeper layers, about 1.4 times higher than the expected ratio from solubility alone. This supports the notion that if anthropogenic climate change continues unabated the oxygen will continue to decrease with a ratio larger than that predicted based on solubility alone, with poorly understood consequences for marine life.

The last part of my thesis was to analyze the interannual to decadal oxygen changes in the North Atlantic. The main reason was that although the previous study focused on long-term changes, the results showed a substantial amount of interannual variability that was not well resolved. Also interesting was the acceleration of the oxygen decrease after the 1990s in some of the isopycnals in the eastern North Atlantic. Moreover, attributions of mechanisms can be better asserted when analyzing data with high spatial and temporal resolution. The individual contributions of the mechanisms controlling the oxygen changes are not yet well understood, nor is it entirely clear whether those changes reflect natural fluctuations or are harbingers of the potential changes lying ahead. For this purpose I analyzed a hydrographic repeated section conducted between 1993 and 2011 along $47^\circ$N in the eastern North Atlantic with almost yearly resolution until 2005. Again the analysis was done on isopycnal layers, and several water masses were identified in the region in the first 1500 dbar: the SPMW between 200−600 dbar, the IW between 500−800 dbar, and the MOW centered at 1000 dbar. The results show that these water masses underwent strong interannual $O_2$ variability with a tendency to decadal ocean deoxygenation from 1993 to 2002 with a magnitude of $-1.8 \pm 0.7 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ in the SPMW, $-2.3 \pm 0.7 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ in the IW and $-1.1 \pm 0.5 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ in the MOW. Weaker changes were found from 2005 and 2011 although the large gap between 2006 and 2009 makes the estimation of the changes unclear and not significant. Some of the interannual changes were driven by mesoscale eddies, these can have a strong impact, as observed for the 2003 section where the observed decrease of AOU (on average $-36 \mu\text{mol kg}^{-1}$) extended until about 1000 dbar and for 379 km. According to our results, the circulation changes are likely to be the main driver for the observed oxygen decrease between 1993 and 2002 in the SPMW and IW. In agreement with the results from Johnson and Gruber (2007) we linked the observed oxygen decrease to the northwestward shift of the Subpolar Front (SF) after 1995 that allowed water of subtropical origin to penetrate into the northeastern regions. This penetration affected SPMW, IW and MOW found in this region. Regarding the SPMW, the oxygen decrease was driven by the replacement of SPMW of subpolar origin, formed at higher densities at the beginning of the observations, with SPMW of subtropical origin formed at lighter densities in 2002. This reduced the ventilation of the SPMW layers and consequently the oxygen concentration.
Moreover, the mixing with IW in the western side also contributed to the oxygen decrease and to the weakening of the high eastern oxygen gradient in the SPMW. At the same time, the IW were also replaced by waters of subtropical origin, probably from a greater contribution in the region of AAIW and MOW that have relatively lower $O_2$ compared to the SAIW. Regarding the MOW we found that changes in $O_2$ concentration were mainly driven by solubility changes, with changes in $O_2$ tending to follow the salinity changes.

In the introductory chapter I presented the NAO as the dominant mode of atmospheric variability in the North Atlantic (Visbeck et al., 2003) (see Fig. 1.8). In the 50-year analysis from 1960 to 2009, it was pointed out that since the decreasing phase of the NAO from high to low positive values is a relatively recent event that started in 1995, the trend of the NAO index over the past 50 years can still be considered positive. Based on this assumption we attempted to relate the observed oxygen changes to the long-term trend in the NAO. Moreover, since the section analysis covers the period during which the NAO shifted between strong positive and low positive phases, also in this latter study we attempted to relate the observed changes with the NAO. Regarding the long-term analysis, we established that the oxygen changes in the LIW and LSW are a consequence of the increase in convection activity in the Labrador Sea after the NAO shifted from strong negative values in 1960s to positive values in the 1990s. This change also caused a warming event of the northern subtropical gyre that is the primary driver for the oxygen decrease in the UW in this region. We established that the same NAO shift can be considered the driver for the decrease in ventilation due to buoyancy forcing, which was the primary driven force for the observed decrease in the oxygen in the MW. However it was not clear if the NAO trend was also linked to the observed oxygen increase in the mode water in the southwestern North Atlantic, and to the difference between the oxygen changes between the eastern and the western regions. In the second study the focus was on the NAO shift between the positive phase in the 1990s and the low positive phase in 2000s. This analysis confirmed that the consistent decrease of oxygen after 1993 was a result of circulation changes, although changes in the buoyancy forcing were not completely excluded.

**Figure 5.1:** This figure from Häkkinen et al. (2011) shows the relationship between the wind-stress curl PC2 (Second Principal Component) in red and the northward transport anomalies of the highest salinity classes ($S>35.4$ in blue and $S>35.4$ in green) at $55^\circ$N.

As previously discussed, the observed circulation changes were attributed to the northward shift of the SF in the eastern North Atlantic as a consequence of the reduced extension of the subpolar gyre. According to Bersch (2002) and Bersch et al. (2007) there is an anti-phase response of the gyre circulation to the NAO shift from positive to negative values. They showed that while in the eastern North
Atlantic the SF shifted northwestward, in the western North Atlantic this front shifted southeastward. The consequences are that while in the eastern North Atlantic subtropical water can penetrate into the northern regions, in the western Atlantic, more subpolar water can penetrate into the southern regions, increasing the freshwater transport and reducing the heat transport. If the northwestward movement of the SF in the eastern North Atlantic due to the NAO shift increases the penetration of subtropical water in the eastern North Atlantic, then it is puzzling why in the 1960s, when the NAO was at its stronger negative phase, the oxygen concentrations were higher than they are today. A recent study from Häkkinen et al. (2011) suggested that the shift of the SF and the associated northward penetration of subtropical water into the northern regions is not directly related to the NAO shift but is a response to the changes in wind-stress curl over the North Atlantic that occur roughly every 15 years. The last shift coincided with the period of my latter study and those of Bersch (2002); Bersch et al. (2007); Johnson and Gruber (2007).

In light of this recent study from Häkkinen et al. (2011), it is possible to hypothesize that in terms of circulation changes the circulation pathway in the 1960s and the 1990s were similar, since as shown in Fig. 5.1 (Häkkinen et al., 2011) the wind-stress curl PC2 (in red) was positive for both periods, while the NAO was negative in the 1960s and positive in the 1990s. In terms of oxygen changes in the 1960s, the high convection in the eastern North Atlantic due to the negative NAO phase produced highly oxygenated water that was advected southward, since the subpolar gyre was expanded southeastward in the eastern North Atlantic due to the positive phase of the wind-stress curl (Fig. 5.2a). In the western North Atlantic, low convection in the Labrador Sea, combined with the northwestward shift of the subpolar front in the Newfoundland Basin, did not allow this lighter flavor of LSW to bring its high oxygen signal into the North American Basin leading to a dominance of southerly low oxygen water (Fig. 5.2a and b). This lighter flavor of LSW was instead deflected toward the eastern regions. Kieke et al. (2009) discussed this light flavor of LSW (defined Upper Labrador Sea Water); they found evidence of this water in the eastern North Atlantic that probably was formed in one of these low convection events before the 1990s. In the 1990s, during the strong positive NAO phase, the situation regarding the ventilation were inverted, i.e. strong convection in the Labrador Sea and low convection in the eastern North Atlantic (Fig. 5.2c). As a consequence the oxygen reduced in the eastern North Atlantic due to reduced ventilation, as observed in the long-term trend (Fig. 5.2d). However, in the 1990s the SF was still shifted southeastward (same situation as the 1960s), thus the circulation could have contrasted the ventilation effect. This is indeed shown in the result of the trend analysis by the fact that the linear trends for the mode and intermediate water in the eastern North Atlantic show increases in the oxygen concentration in the 1990s. However since the wind-stress curl (Fig. 5.1) shifted from positive to negative values after the 1990s, (Fig. 5.2e) the subpolar gyre shifted northwestward causing the penetration of subtropical water to the north in the eastern North Atlantic and the spreading of more subpolar water to the south in the western North Atlantic (Fig. 5.2e and f).

This effect can be the reason for the observed acceleration of the oxygen decrease in the mode and intermediate water observed in both analyses, and it can be also the cause of the observed oxygen increase in the North American Basin. Although the western basin was not considered in my second analysis, I computed the oxygen difference between 1993 and 2002 along the A2 transect that crosses the Atlantic from the Newfoundland Basin to the eastern margin of the Western European basin (Fig. 5.3). Figure 5.3 shows that while the Western European basin lost oxygen from 1993 to
Figure 5.2: (a, c and e): Schematic sketch of the combined effect of the NAO oscillation on the ocean ventilation (blue and red patches), and the Wind-stress curl on the ocean circulation (orange and dashed red arrows for surface circulation and blue and red arrows for deep circulation, dark red is the MOW pathway). In a) the schematic for the 1960s, when the NAO was strong negative and the wind-stress curl was positive. In c) the schematic for the 1990s when the NAO was strong positive and the wind-stress curl positive. In e) the schematic for 2000s when the NAO was in its low positive and sometime negative phase and the wind-stress curl was negative. (b, d and f) are the resulting effect on the oxygen concentration in the density range occupied by mode and intermediate waters.

2002, the Newfoundland Basin gained oxygen. This is a further confirmation that the oxygen changes are strongly sensitive to circulation changes.

Indeed the oxygen increase in the Newfoundland Basin can be linked to this anti-phase response to the wind-stress curl of the western and eastern basins. While the eastern part lost oxygen because
5.1 Caveats and Outlook

Although I was able to compute trends for almost 50 years for the long-term analysis, this was not a long enough period to distinguish between the changes driven by natural climate oscillation and anthropogenic climate forcing. This suggests a need to continue with oxygen sampling efforts in order to improve our temporal and spatial coverage. In this regard, I strongly believe that proposed projects such as the Argo-oxygen floats would be extremely helpful to improve the future monitoring of long-term trends. As mentioned in the previous section, there is a tremendous amount of oxygen data that could be potentially used to further increase the temporal and spatial coverage after the application of some corrections. This is certainly something that was missed in this analysis and that affected some of the results, as the scarcity of the data led to non-significance of trends in some regions. When I selected the cruises from the WOD05 I excluded all data collected before 1960, based on the assumption that before the 1960s the methods used for oxygen sampling were of lower accuracy. However this was

Figure 5.3: $\sigma_1$-longitude 2002–1993 difference section of $O_2$ (µmol kg$^{-1}$) displayed along the A2 section from 44°W to 12°W.

of the entrance of subtropical water, the western regions gained oxygen due to the entrance of more oxygenated water of subpolar origin. Further investigations are needed to confirm this hypothesis; in particular the relative contributions of the changes in circulation and changes in ventilation are not yet clear, although it seems that both mechanisms cause oxygen changes in the eastern and western North Atlantic of opposite direction. This is also an interesting aspect revealed by both analyses, since oceanic climate models have predicted a more homogeneous decrease in the oxygen concentrations in future projections if global warming continues unabated.
an arbitrary choice, and given the necessity to extend the data coverage it would probably be useful to include pre-1960s data.

To compute the $O_{2}$sat and consequently the AOU I used the equation from Weiss (1970), nevertheless other equations could have been used. Garcia and Gordon (1992) recommended using another equation that gives more precise results. However, they also argued that when relatively high precision of $O_{2}$sat is not required, it makes no difference which $O_{2}$ solubility formula is used, since the values estimated from these formulas agree to within an rms deviation of $\pm 0.3\%$ ($\pm 1.01 \mu mol \text{ kg}^{-1}$). The changes we observed are, however, higher than this estimation. Moreover, to be consistent I recalculated the AOU for all data, including data from the CARINA and GLODAP datasets where these parameters were already computed using a different equation.

The $O^*_2$ was computed using the phosphate measurements available from the three datasets. However, although a quality control on this nutrient was done in the CARINA and GLODAP datasets, this was not the case for the WOD05. Indeed, as I explained the WOD05 cruises were selected based on the quality of the oxygen data, and no check was performed to assert the quality of the nutrients data. This needs to be taken into account when using this parameter in the analysis.

In the second analysis I used several repeated hydrographic transects to investigate the interannual and decadal variability of the oxygen. I applied a filter based on a moving average of 160 dbar on the PV profiles. Smoothing of CTD profiles are necessary to remove the noises of such a high resolution profile, however, the filter applied to the PV was probably too high and it could have been enough to apply only 80 dbar filtering. This might results in a bias due to the strong smoothing, however, I believe that this did not compromise the qualitative analysis based on the assumption that increase in PV through time leads to decrease of ventilation.

Although this study was useful to better understand the driving mechanisms of the oxygen changes in the eastern North Atlantic from 1993 to at least 2002, I was not able to completely understand the driving mechanisms for the changes observed after this time period. The main reason was the temporal gap between 2006 and 2009. Nevertheless, I believe that these kinds of analyses are extremely useful since it is possible to observe changes in ocean properties through time with extremely high vertical resolution. However, to better understand if the observed changes are the results of changes in the properties of the water masses at the source or due to changes in the pathway and spreading of the water masses, it would be useful to have other sources of data independent from what is provided by the hydrographic sections, for example by integrating the results with floats, moorings and satellites altimetry data.
Bibliography


Appendix A

Supplementary material: Chapter 3
This appendix provides the supplementary materials that will be available online for the paper submitted to the *Journal of Geophysical Research*.

This supplementary material provides additional information about the data distribution in the region of study and the additional statistical methods used to support our trend analyses.

Figure A.1 shows the data distribution by layer and region giving an overview of the temporal coverage for each analyzed $\sigma_1$ layer.

Figures A.2, A.3 and A.4 illustrate the robustness of our ordinary least-squares linear regression-based trend analyses by comparing it to other statistical methods to determine the $O_2$ trends. Figure A.2 investigates the sensitivity of the trends with respect to our annual averaging of the data. To this end, we conducted a bootstrapping analysis, for which we created 1000 new time-series for each $\sigma_1$ level with the same number of annual points as the original time-series, but where years with more than one observation were represented by a randomly selected value rather than the mean. We then computed the trends of each time-series and determined the median and the 95% confidence interval from the cumulative distribution of the slopes. This method gave very similar values, indicating that the trends and uncertainties computed from the annual mean oxygen for each year is robust.

In Figure A.3 we compare the linear-regression trends with those determined by computing the difference between the mean oxygen value of all data from 1990 to 2005 and the mean value of all observations from 1960 to 1975. This method is less sensitive to the values at the beginning or end of the time-series, but requires a relatively even coverage of the data within these two 15 years periods. This is fulfilled for almost all the regions except for the LS and some shallower layers (Figure A.1).

Finally, Figure A.4 compare the linear-regression trends with those based on the Theil-Sen method (Sen, 1968; Theil, 1950). This non-parametric method is more robust with regard to outliers (e.g., Fernandes and Leblanc (2005)) as it computes the trends by determining the median of the slopes between all data pairs. This also gave very similar results to those inferred from the standard linear regression model.

We computed the trends and concentration changes for each water-mass horizon using two separate methods. First, we used the linear trends computed for each isopycnal layer and averaged them in a weighted manner over the water mass, with the weights stemming from the volumes of the isopycnal layers that make up the five horizons. The uncertainties were determined by quadratic (Gaussian) propagation of the standard error of the trend and the significance determined by a Student-t test at the 95% confidence level. In the second method, we determined the trend directly for the entire watermass horizon using all data within this horizon. To this end, the mean concentration on each layer was first subtracted to form an anomaly, which were then combined across the entire horizon for the trend analysis. The results of these two methods are compared in Tables A.1 and A.2.

From Figure A.5 to Figure A.13 all the linear trends computed for the eight regions are displayed.
Table A.1: $O_2$ changes over the last 49 years ($\mu$mol kg$^{-1}$) for the UW, MW and IW water masses computed by i) averaging the linear trends over all isopycnal layer of a particular water mass (Averaging method) or by ii) first removing the mean value of all data on each isopycnal layer and then computing the trend of the resulting anomaly data using all data within a water mass at once (Anomaly method). The numerical values reported in this paper come from the first method.

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Table A.2: As Table A.1, but for the O\textsuperscript{2} changes in the LIW and LSW water masses.

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2.2 Number of samples for oxygen by year in CARINA-ATL.

2.3 Maps showing the temporal distribution (5 year intervals) of stations that have oxygen samples in the final product of CARINA-ATL (without the 6 reference cruises from GLODAP, see Sect. 2): (a) 1977 to 1981; (b) 1982 to 1986; (c) 1987 to 1991; (d) 1992 to 1996; (e) 1997 to 2001, and (f) 2002 to 2007.

2.4 Overview of the oxygen distribution in the dataset depicted as vertical profiles for 11 separate regions: (a) 70°N–46°N and 80°W–30°W, (b) 70°N–46°N and 30°W–20°E except the cruises in the Arctic Ocean north of 60°N, (c) 46°N–23°N and 80°W–40°W, (d) 46°N–23°N and 40°W–0° (e) 23°N–EQ and 80°W–40°W, (f) 23°N–EQ and 40°W–0° (g) EQ–23°S and 60°W–20°W, (h) EQ–23°S and 20°W–20°E (i) 23°S–46°S and 60°W–20°W, (j) 23°S–46°S and 20°W–20°E, (k) 46°S–70°S and 60°W–20°W. Shown in gray is the vertical distribution for the entire North Atlantic (a, b, c, d, e and f) and the entire South Atlantic (g, h, i, j and k) respectively. Shown in red is the vertical distribution in the area where the panel is located on the map from 1997 to 2007, in blue is the vertical distribution from 1987 to 1996 and in green is the vertical distribution from 1977 to 1986. The black line is the mean profile of the entire data in that area interpolated with a piecewise Cubic Hermite Interpolating scheme. Oxygen units are in \( \mu \text{mol kg}^{-1} \).

2.5 Plot of the offsets calculated for each crossover in the final product of CARINA-ATL after adjustments have been applied. WL: the weighted mean of the offsets; F: the percentage of offsets indistinguishable from 1 within their uncertainty; L: the number of crossovers.
2.6 Plot of the offsets for each crossover (red dots) and their uncertainties (black error bars). The offsets from the reference cruises are also included in the figure. The first row, i.e. (a–d) corresponds to the results before any suggested adjustment have been applied, while the second row, i.e. (e–h) corresponds to the results after the manually edited adjustments were applied. First column, i.e. (a) and (e), show the results from the offset analysis ordered by offset. The second, third, and forth columns depict the offsets after the inversions. (b) and (f) are results from the Simple least Square method (SLSQ), (c) and (g) are results from Weighted Least Square method (WLSQ), and (d) and (h) are results from the Weighted Damped Least Square method (WDLSQ). The red numbers in the upper-left corner of each panel are the percentage of crossovers that are statistically indistinguishable from zero.

2.7 Plot of the individual cruise corrections and their uncertainties based on the WDLSQ method (see Table 2.1). In black are the corrections before any adjustment has been applied, i.e. the results from the first inversion of the offset results. In red are the corrections that the WDLSQ inversion suggests after the manually edited adjustments were applied to the oxygen data (see Table 2.1). The thin black lines represent the threshold of 1% of allowed adjustments. Cruises for which only red symbols are shown did not change their cruise adjustment from the initial to the second inversion. Cruises for which only black symbols are shown are those whose oxygen data have been flagged as questionable and deleted in the adjusted dataset.

3.1 a) Map of the North Atlantic showing the stations contained in the different data sets (green for WOD05, blue for GLODAP, violet for CARINA, and red for the cruise MSM12/3). Also shown are the eight regions: LS (Labrador Sea), IS (Irminger Sea), IB (Iceland Basin), RT+WEBn (Rockall Trough and Western European Basin North), NFL (Newfoundland Basin), NAB (North American Basin), MAR (Mid Atlantic Region), and WEBs (Western European Basin South). b) Number of observations per year in the different data sets within the North Atlantic region shown in a.

3.2 Isopycnal oxygen trends from 1960 through 2009 for the 8 analyzed regions. The colors of the lines correspond to the colors of the regions. The shading around each lines represents the trend ± 2 standard deviation (2σ). The gray boxes represent the σ1-based density horizons in defined in this study: UW (Upper Water), MW (Mode Water), IW (Intermediate Water), LIW (Lower Intermediate Water), and LSW (Labrador Sea Water).

3.3 As Figure 3.2, but for the negative of the apparent oxygen utilization (-AOU).

3.4 As Figure 3.2, but for the oxygen saturation concentration, O₂sat.
3.5 Weighted mean $O_2$ concentration changes over the last 49 years for the five horizons and their drivers. The first column (a, d, g, j and m) show the changes in oxygen, while the second (b, e, h, k, and n) and third columns (c, f, i, l and o) show the changes induced by solubility (represented by the $\Delta O_2^{sat}$) and by changes in circulation/ventilation and remineralization (represented by the $-\Delta AOU$), respectively. The rows show the results for the different water masses: UW: a, b, c; MW: d, e, f; IW: g, h, i; LIW: j, k, l; LSW: m, n, o). Statistically significant concentration changes are represented with filled circles, while the not significant ones are plotted with open circles.

3.6 As Figure 3.5, but for the gas-exchange component of oxygen, i.e., $O_2^{*}$. Regions with insufficient data are shaded in grey.

3.7 Timeseries of trends in oxygen and its components for selected regions of the mode-water density horizon. The first row, i.e., panels a), b) and c) show trends for $O_2$, the second row, i.e., panels d), e) and f) those for $O_2^{sat}$, and the third row, i.e., panels g), h) and i) those for $O_2^{*}$. Actually plotted are the anomalies relative to the long-term mean on each of the isopycnal layers that contribute to the mode-water density horizon. The first column, i.e., panels (a), d) and g) depict the results for the RT+WEBn region. The second column, i.e., panels b), e), and h) depict the results for the WEBs region. The third column, i.e., panels c), f) and i), depict the results for the NAB region. The symbols are the anomaly from the median value of the linear trend for each isopycnal layer that forms the MW horizon, while the thick line is the linear trend. In the lower left corner is the trend with the uncertainty in $\mu$mol kg$^{-1}$ decade$^{-1}$.

3.8 As Figure 3.7, but for selected regions for the intermediate water horizon. Shown are the results for the IB region (panels a), d) and g)), the WEBs region (panels b), e), and h), and the MAR region (panels c), f) and i).

3.9 As Figure 3.7, but for selected regions for the Labrador Sea Water horizon. Shown are the results for the LS region (panels (a, d) and g)), the IB region (panels b), e), and h), and the WEBs region (panels c), f) and i).

3.10 As Figure 3.5, but for vertically and temporally integrated changes in oxygen and in its components, i.e., $\Delta O_2^{sat}$ and $-\Delta AOU$.

4.1 Simplified circulation sketch of the upper and intermediate North Atlantic circulation superimposed on the North Atlantic Mean Dynamic Ocean Topography (1992-2002) (Maximenko et al., 2009). Contoured as black lines is the topography derived from the TerrainBase gridded at 5-minute intervals. Red and orange arrows shows the circulation pathway of the NAC, the shade area indicates the SPMW associated with the NAC based on (Brambilla and Talley, 2008); in green are the paths for the IW (Schmitz, 1996; Pollard et al., 2004) and in dark red the northward path of the MOW (Lozier and Stewart, 2008). The black lines represents the cruise track for the A2 and 47°N transects. The rectangle highlights the region of this study.
4.2 Climatological oxygen distributions at $\sigma_1 = 31.65$ a), $\sigma_1 = 31.80$ b) and $\sigma_1 = 32.10$ c) corresponding to the centers of SPMW, IW and MOW (from WOCE climatology (Gouretski and Koltermann, 2004)). In all the sketches the black lines show the location of transects in the eastern part of the North Atlantic. 

4.3 Mean pressure-longitude sections along the hydrographic section of salinity a), oxygen b) and Potential Vorticity (PV) c). Contour lines are the potential $\sigma_1$ contoured at 0.05 interval, thick contour lines indicates the isopycnals for SPMW ($31.55 \leq \sigma_1 < 31.75$), IW ($31.75 \leq \sigma_1 < 31.90$) and MOW ($31.90 \leq \sigma_1 < 32.2$). Data are first interpolated on a regular $\sigma_1$ grid and then averaged along pressure.

4.4 $\sigma_1$-Longitude distribution for AOU ($\mu$mol kg$^{-1}$) displayed along the eastern part of 47°N/A2 section for the period 1993–2011. AOU is displayed as the particular deviation from the mean AOU distribution derived from averaging all available sections. The sections are masked for the winter outcrop, computed with the winter surface $\sigma_1$ from the WOA09 and represented by the black dashed line. Black contours lines denote pressure in dbar, pressure below 1500 dbar and less than 100 dbar are excluded.

4.5 Hovmöller diagram showing the time evolution of $O_2$ a), $\theta$ b), PV c), AOU d), Salinity e) and pressure f), along 47°N for the SPMW. The density range for the SPMW is $\sigma_1 = 31.55$-$31.75$ kg m$^{-3}$. Shades show years with missing data. In the lower panels it is shown the topography and the $\sigma_1$ density range on a pressure grid of SPMW. Please notice non linear color scale for $O_2$, AOU and PV.

4.6 Time evolution of $O_2$ ($\mu$mol kg$^{-1}$) a–d, AOU ($\mu$mol kg$^{-1}$) e–h, and PV ($10^{-12}$ m$^{-1}$ s$^{-1}$) i–l, along isopycnals ($\sigma_1$). The black lines indicate the density ranges of SPMW, IW and MOW. Shaded rectangles indicate years with missing data.

4.7 Time evolution of salinity a–d, $\theta$ (°C) e–h, and pressure (dbar) i–l, along isopycnals ($\sigma_1$). The black lines indicate the density ranges of SPMW, IW and MOW. Shaded rectangles indicate years with missing data.

4.8 Trends for oxygen, layer thickness, AOU, PV, salinity and pressure for the SPMW (in red) (from 25°W to 12°W), IW (in blue) (from 30°W to 12°W) and MOW (in black) (from 30°W to 12°W). Gray shades highlights years with missing data.

4.9 Hovmöller diagram showing the time evolution of $O_2$ a), $\theta$ b), PV c), AOU d), Salinity e) and pressure f), along 47°N for the IW. The density range for the IW is $\sigma_1 = 31.75$-$31.9$ kg m$^{-3}$. Shades show years with missing data. In the lower panels it is shown the topography and the $\sigma_1$ density range on a pressure grid of IW. Please notice non linear color scale for $O_2$, AOU and PV.

4.10 Hovmöller diagram showing the time evolution of $O_2$ a), $\theta$ b), PV c), AOU d), Salinity e) and pressure f), along the longitude for the MOW. The density range for the MOW is $\sigma_1 = 31.9$-$32.2$ kg m$^{-3}$. Shades show years with missing data. In the lower panels it is shown the topography and the $\sigma_1$ density range on a pressure grid of MOW. Please notice the non linear color scale for $O_2$, AOU and PV.
4.11 In a) it is shown the gridded absolute topography as a weekly average centered on the 20th of August 2003, corresponding to the date of the stations marked with the white open circle. Note, although the red-blue color bar, the map represents absolutes values. Below is the oxygen b), salinity c) and $\theta$ d) sections. The oxygen section is further zoomed in the lower panel e). White line and triangles show the location of the station with the mode-water eddy (red triangle) and the station with the cyclonic eddy (blue triangle). Oxygen, salinity and temperature profiles of these eddy stations are shown on panels f), g) and h). .......................... 89

5.1 This figure from H"akkinen et al. (2011) shows the relationship between the wind-stress curl PC2 (Second Principal Component) in red and the northward transport anomalies of the highest salinity classes ($S>35.4$ in blue and $S>35.4$ in greed) at $55^\circ$N. .... 100

5.2 (a, c and e): Schematic sketch of the combined effect of the NAO oscillation on the ocean ventilation (blue and red patches), and the Wind-stress curl on the ocean circulation (orange and dashed red arrows for surface circulation and blue and red arrows for deep circulation, dark red is the MOW pathway). In a) the schematic for the 1960s, when the NAO was strong negative and the wind-stress curl was positive. In c) the schematic for the 1990s when the NAO was strong positive and the wind-stress curl positive. In e) the schematic for 2000s when the NAO was in its low positive and sometime negative phase and the wind-stress curl was negative. (b, d and f) are the resulting effect on the oxygen concentration in the density range occupied by mode and intermediate waters. ............................................. 102

5.3 $\sigma_1$-longitude 2002–1993 difference section of $O_2$ ($\mu$mol kg$^{-1}$) displayed along the A2 section from 44$^\circ$W to 12$^\circ$W. .......................... 103

A.1 Isopycnal distribution of the oxygen data (square symbols) in the eight regions over the 49 years of observation. .......................... 119

A.2 Isopycnal oxygen trends from 1960 through 2009 for the 8 analyzed regions. The colors of the lines correspond to the colors of the regions and represent the linear trends. The blue lines in the foreground represent the results from the bootstrapping analysis. The colored shading around each line indicate the trend $\pm 2$ standard deviation ($2\sigma$), while the blue shading represents the 95% confident intervals from the cumulative distribution of the slopes computed with the bootstrapping. The grey boxes represent the $\sigma_1$-based water mass horizons defined in this study: UW (Upper Water), MW (Mode Water), IW (Intermediate Water), LIW (Lower Intermediate Water), and LSW (Labrador Sea Water). .......................... 120

A.3 As Fig.A.2 except for the blue lines representing the trends computed by differencing the mean oxygen value of all data from 1990 to 2005 from the mean value of all observations from 1960 to 1975. The blue shading indicates the $\pm 2$ standard deviation ($2\sigma$) around this trend. .......................... 121
A.4 As Fig. A.2 except for the blue lines representing the trends determined by the Theil-Sen method. The blue shading around each blue lines indicates the 5 to 95% confidence interval determined from the cumulative distribution of the pair-wise trends.

A.5 Timeseries of trends in oxygen and its components for the southern regions of the UW density horizon. The first row shows trends for $O_2$, the second row those for $O_{sat}^2$, and the third row those for $O_{*}^2$. Actually plotted are the anomalies relative to the long-term mean on each of the isopycnal layers that contribute to the UW density horizon. The first column depicts the results for the NAB region. The second column depicts the results for the NFL region. The third column depicts the results for the MAR region. The fourth column depicts the results for the WEBs region. The symbols represent the anomaly from the median value of the linear trend for each isopycnal layer that forms the UW horizon, while the thick line is the linear trend determined by the ordinary least-squares regression method. The trend with its uncertainty in $\mu$mol kg$^{-1}$ decade$^{-1}$ is shown in the lower left corner. Linear trends were computed only for those water masses and regions where the data coverage was sufficient.

A.6 As Figure A.5, but for the northern regions of the MW water mass horizon. Shown are the results for the IB and the RT+WEBn regions.

A.7 As Figure A.5, but for the southern regions of the MW water mass horizon. Shown are the results for the NAB, NFL, MAR and WEBs regions.

A.8 As Figure A.5, but for the northern regions of the IW water mass horizon. Shown are the results for the LS, IS, IB and RT+WEBn regions.

A.9 As Figure A.5, but for the southern regions of the IW water mass horizon. Shown are the results for the NAB, NFL, MAR and WEBs regions.

A.10 As Figure A.5, but for the northern regions of the LIW water mass horizon. Shown are the results for the LS, IS, IB and RT+WEBn regions.

A.11 As Figure A.5, but for the southern regions of the LIW water mass horizon. Shown are the results for the NAB, NFL, MAR and WEBs regions.

A.12 As Figure A.5, but for the northern regions of the LSW water mass horizon. Shown are the results for the LS, IS, IB and RT+WEBn regions.

A.13 As Figure A.5, but for the southern regions of the LSW water mass horizon. Shown are the results for the NAB, NFL, MAR and WEBs regions.
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